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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

10 Mar 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-063**

[redacted] Capt. Rene I. Gonzale~~z, Ph~~D, "Review of POSS Effects on Polymers"

Lab Visitors and Scientists Briefing
(Deadline: 14 Apr 2003)

(Statement A)

REVIEW OF POSS EFFECTS ON POLYMERS AND THE FUTURE 6.1 RESEARCH DIRECTION OF THE POSS PWG

AFOSR Review for

Dr. Charles Y-C Lee

13 December 2002

Capt. Rene I. Gonzalez, Ph.D.
Project Leader
POSS-Polymer Working Group
Air Force Research Laboratory
(661)275-5252
rene.gonzalez@edwards.af.mil

OVERVIEW

I. POSS Programs/ People

II. What is POSS and why use it?
  - a) POSS polymer incorporation
  - b) Theorizing a POSS Model
  - c) Why POSS in not just a sphere & the importance of R
  - d) POSS synthesis / Cage variation

III. Quantitatively, What does POSS do in different polymer systems? (Our and Collaborators work / Including Highlights from the POSS Conference)
  - a) Semicrystaline Polymers (Polyethylenes, PEO, PET)
  - b) Blends
  - c) Rubbers and TPE's (PN, Kraton)
  - d) Glassy Polymers (Polystyrene, PMMA)
  - e) Thermosets
  - f) Polyimides Space-Survivability AO Results

IV. POSS Lubricants

V. Plan for refocusing our AFOSR sponsored 6.1 effort

Polymer Working Group - Research

Basic R&D (6.1) PROGRAMS AFOSR

POSS Synthesis and Characterization
POSS Polymer Processing
POSS for Space-Survivable Materials

↓

Applied R&D (6.2) PROGRAMS AFRL

Solid Rocket Motor Insulation/Casing
Liquid Rocket Engine Ducting
High Temp Lubes/Jet Canopies/Radomes

↓

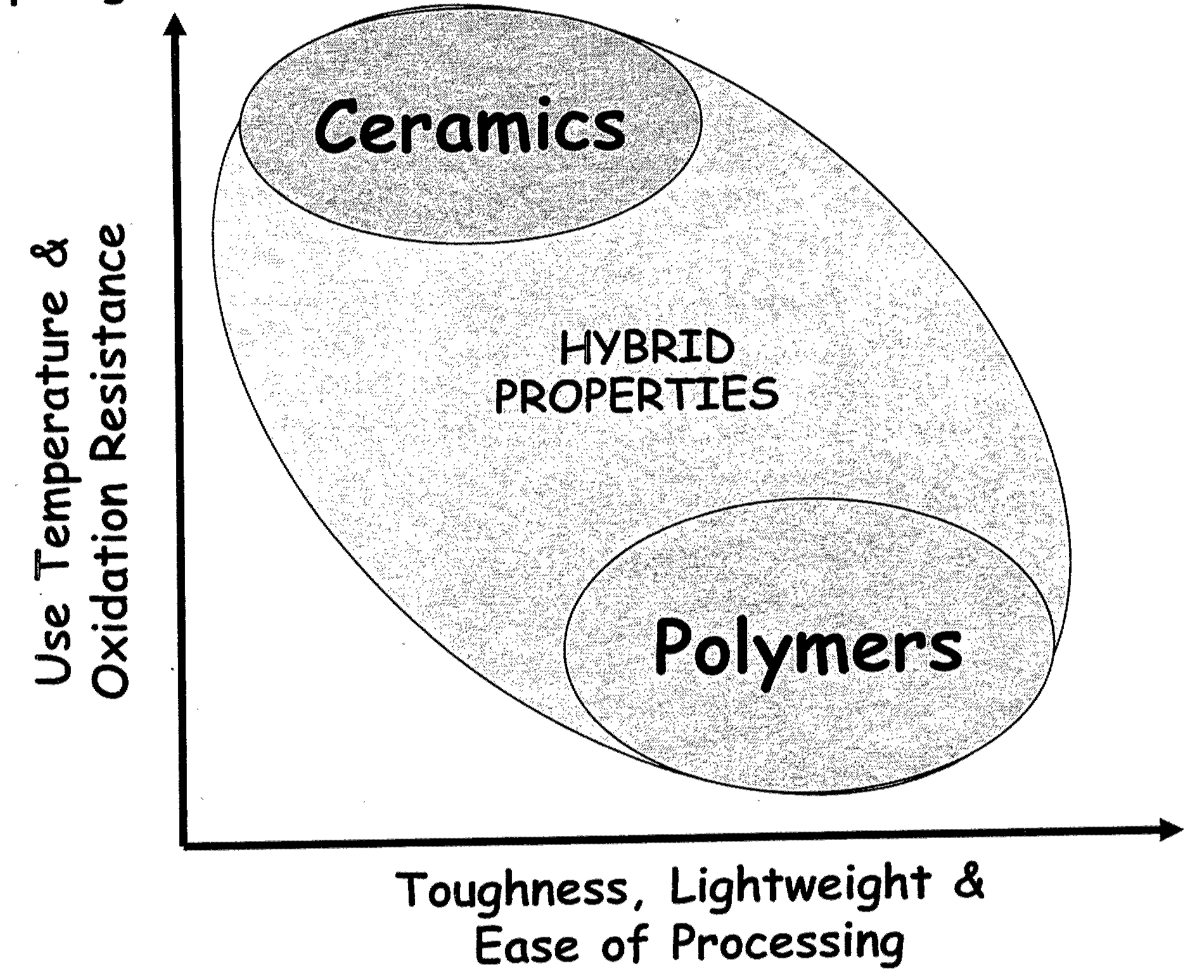
Technology Transfer

AFRL/PRSM People and Projects

Dr. Tim Haddad: Mr. Brian Moore	Basic R&D - POSS size and R group effects, reactivity ratios Appl. – Thermosets, POSS-polymers
Dr. Rusty Blanski: Mr. Delbert Jung	Basic R&D - POSS blends and additives Appl. – Lubricants, Rocket Motor Insulation
Dr. Brent Viers:	Basic R&D - Surface Science/Mechanical Properties, Li Batteries Nanotechnology POC for Propulsion Directorate Appl. - Coatings/Surface Properties, Mech. Tests
Mr. Patrick Ruth:	Basic R&D - Polymer processing, Blending Appl. - All Processing, Insulation, Electronic Encapsulants
Capt. Rene Gonzalez: Dr. Sandra Tomczak:	Basic R&D - Polymer Synthesis/Characterization, AO resistance, surface degradation, reactivity studies, POSS-Polyimides Appl. – Space Survivable Materials
Dr. Joe Mabry Mrs. Becky Morello	Basic R&D - High performance polymers, POSS Lubricants Appl. - LRE ducting tubing/Insulation
Dr. Shawn Phillips	Branch Chief

Hybrid Inorganic/Organic Polymers

Goal: Develop High Performance Polymers that REDEFINE material properties

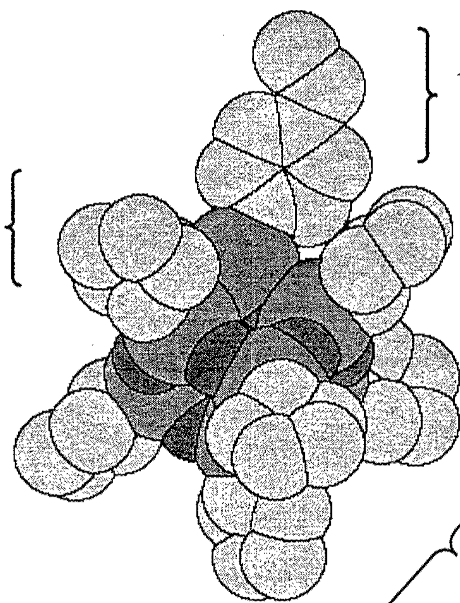


- Hybrid plastics bridge the differences between ceramics and polymers

Anatomy of a POSS Nanostructure

Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.



May posess one or more functional groups suitable for polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

Why POSS and Why Nano?

1 mm
- Sewing Needle
- Razor Blade Thickness

100 μm
- Human Hair
- Most Cells & Fibers

10 μm

1 μm
- Bacteria, Fillers & Polymer Morphology

100 nm
- Viruses & Nanofillers

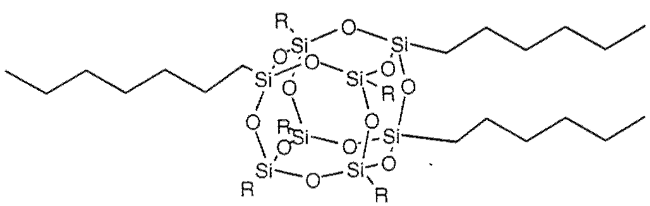
10 nm
- POSS® Building Blocks
- Macromolecules

1.0 nm
- Atoms / Small Molecules

0.1 nm

Field	Property	Critical Length
Electronics	Tunneling	1-100 nm
Optical	Quantum Well	1-100 nm
	Wave Decay	10-1000 nm
Polymers	Primary Structure	0.1-10 nm
	Secondary Structure	10-1000 nm
Mechanics	Dislocation Interaction	1-1000 nm
	Crack Tip Radius	1-100 nm
	Entanglement Rad.	10-50 nm
Therm-Mech.	Chain Motion	0.5-50 nm
Nucleation	Defect	0.1-10 nm
	Critical Nucleus Size	1-10 nm
	Surface Corrugation	1-10 nm
Catalysis	Surface Topology	1-10 nm
Biology	Cell Walls	1-100 nm
Membranes	Porosity Control	0.1-5 nm

POSS Polymer Incorporation



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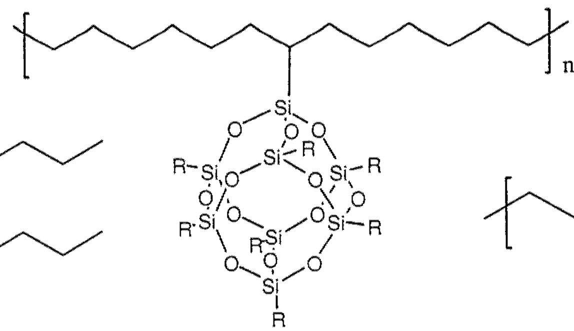
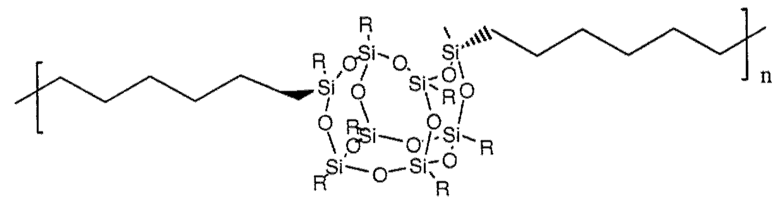
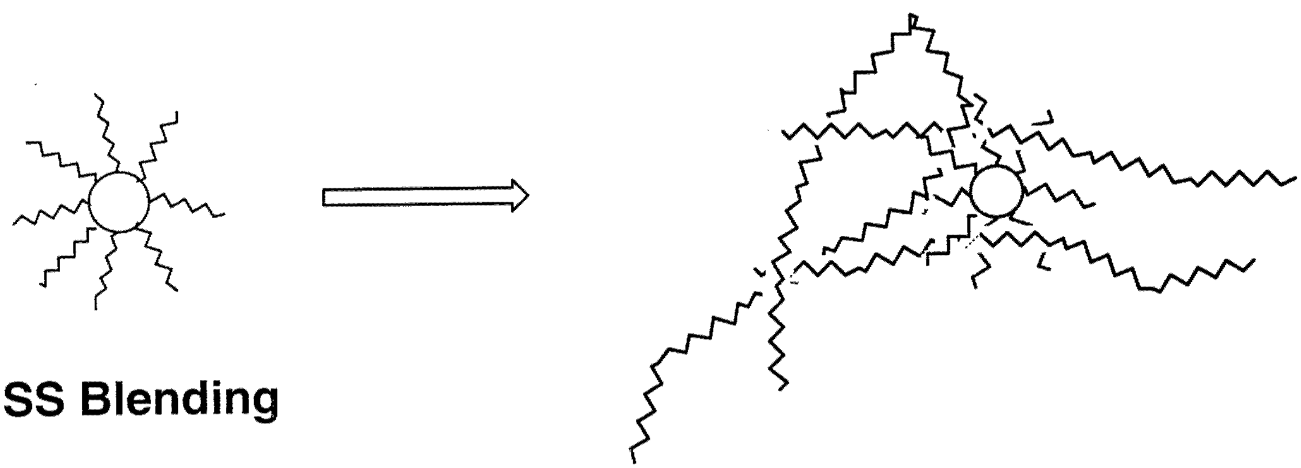


Pendant Polymer



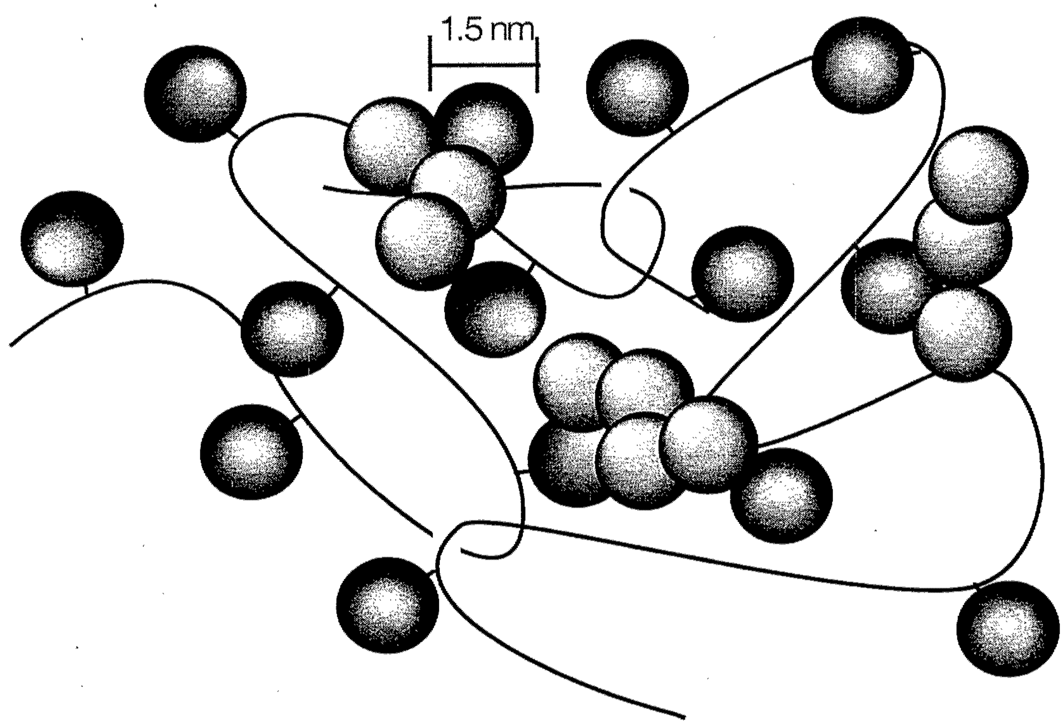
Bead Copolymer

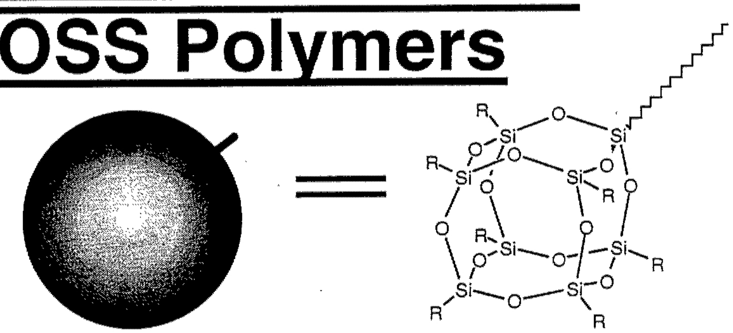


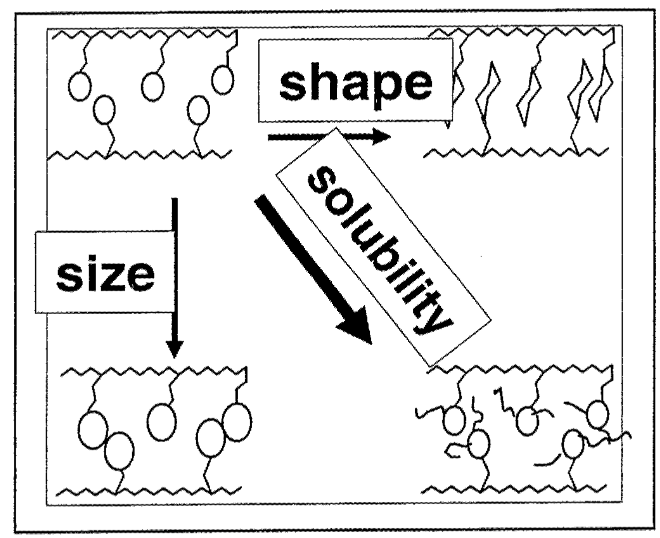
POSS Blending

Structure/Property Relationships

Conceptual Model for POSS Polymers







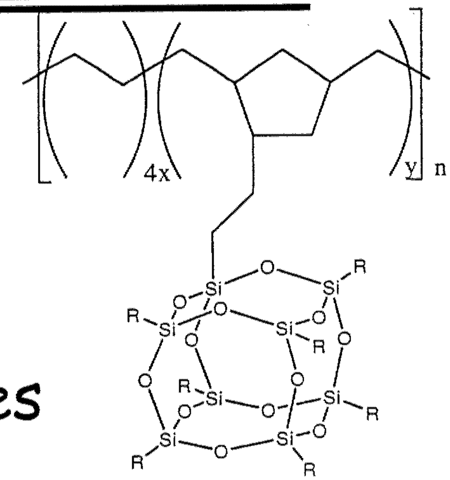
POSS-POSS interactions?
Entanglement?
Aggregation?

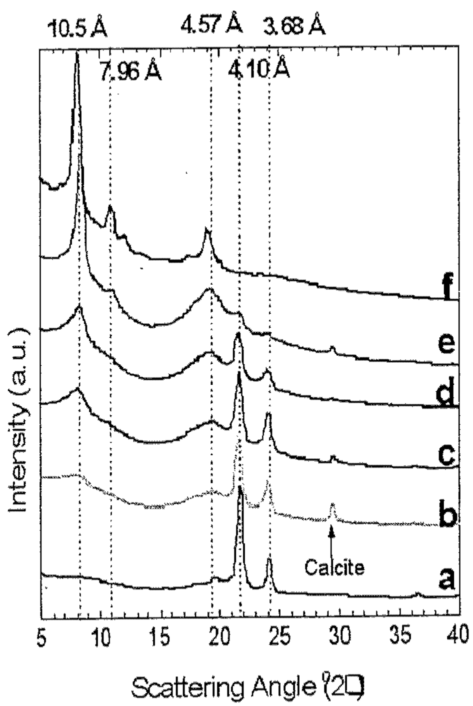
Maximizing property enhancements through changes at the nano level

- Polymer compatibility vs. POSS/POSS interactions

Coughlin Model for POSS Polymers

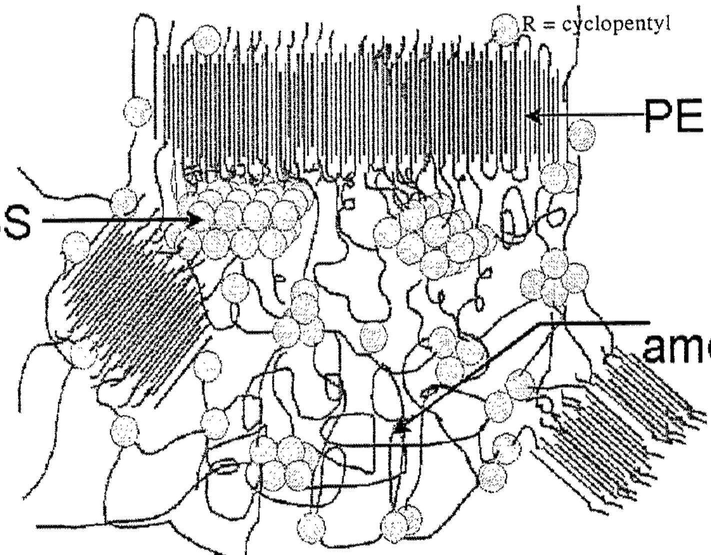
POSS-Polyethylenes
Dual crystalline system with limited crystallization
-chain folded PE lamellae
-2 dimensional raft/sheet like POSS structures





Line Profiles of Wide-angle X-ray Scattering Data of PE-POSS Copolymers.

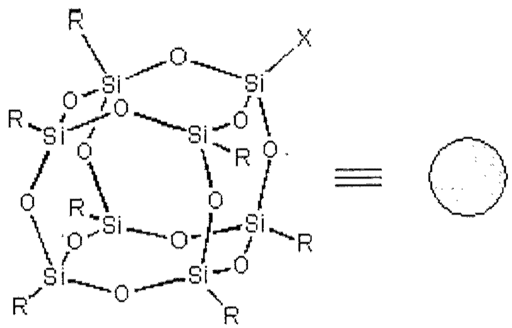
(f) POSS Monomer
(e) PE+56wt% POSS
(d) PE+37wt% POSS
(c) PE+27wt% POSS
(b) PE+19wt% POSS
(a) PE



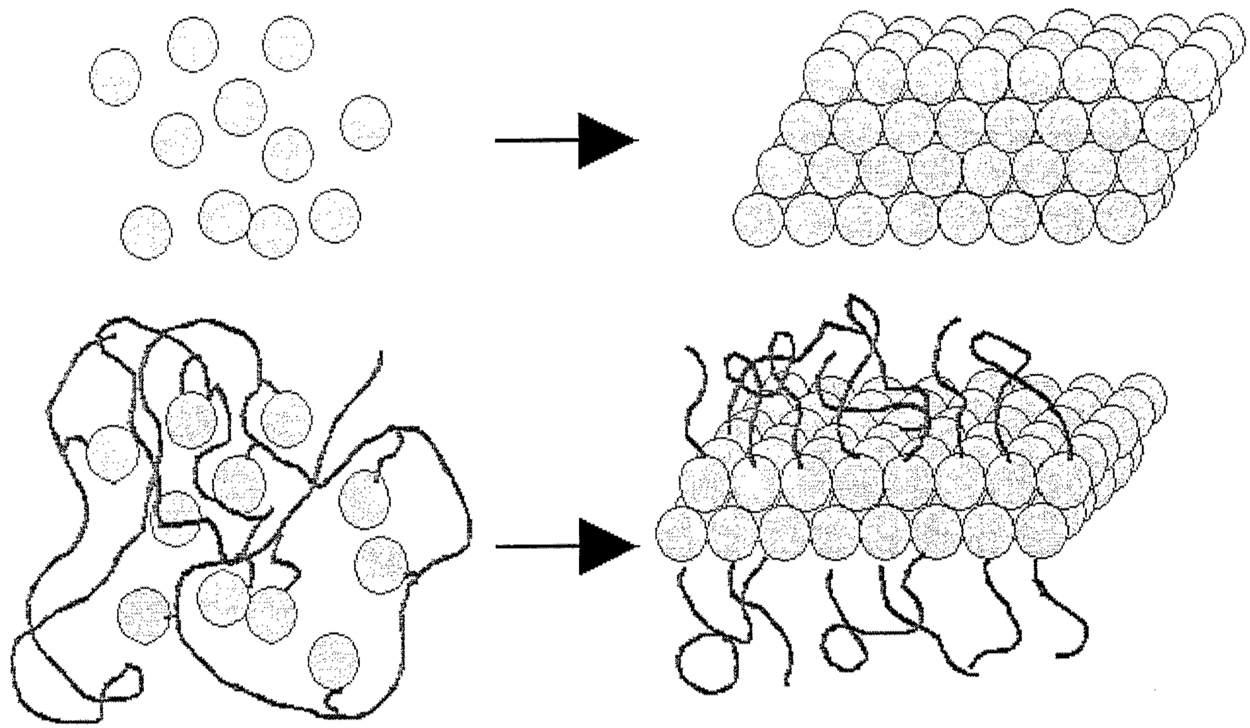
Macromolecules 2002, *35*, 2375-2379

Bryan Coughlin-UMass

Coughlin Model for POSS Polymers Continued

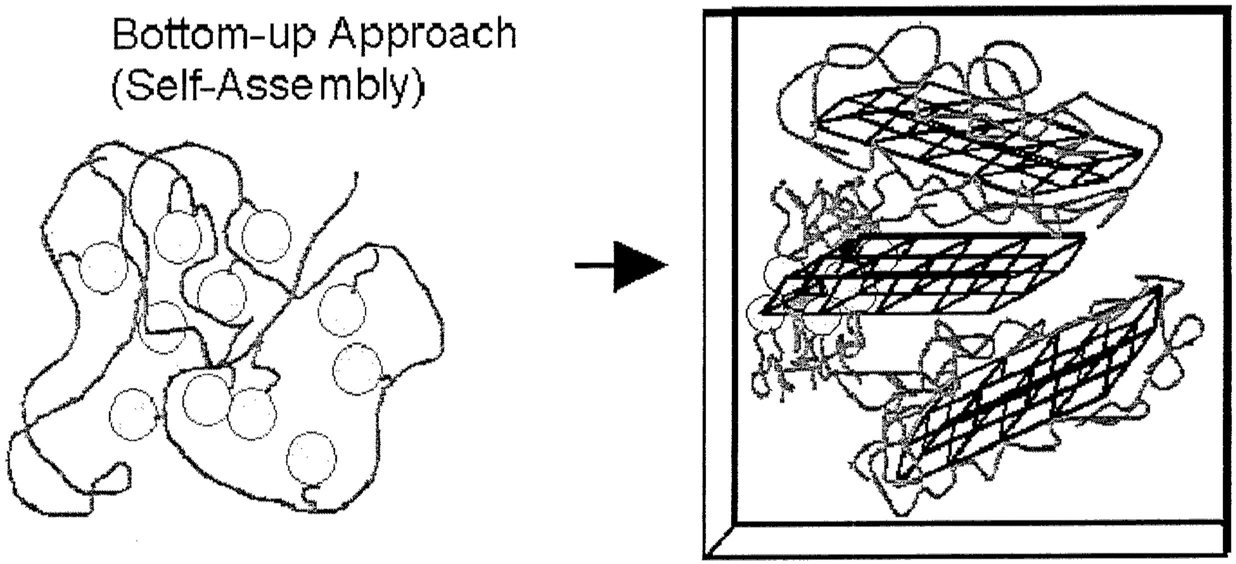


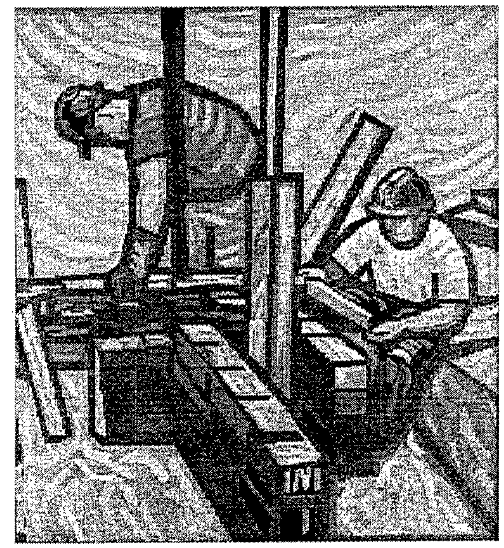
As a solid by itself, POSS crystallizes
As a tethered solid POSS can form 2-dimensional rafts



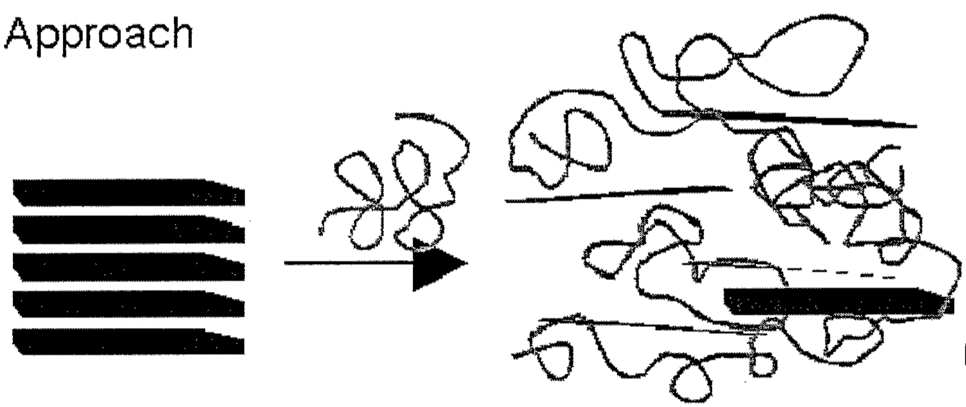
Coughlin Model for POSS Polymers Continued

Bottom-up Approach
(Self-Assembly)



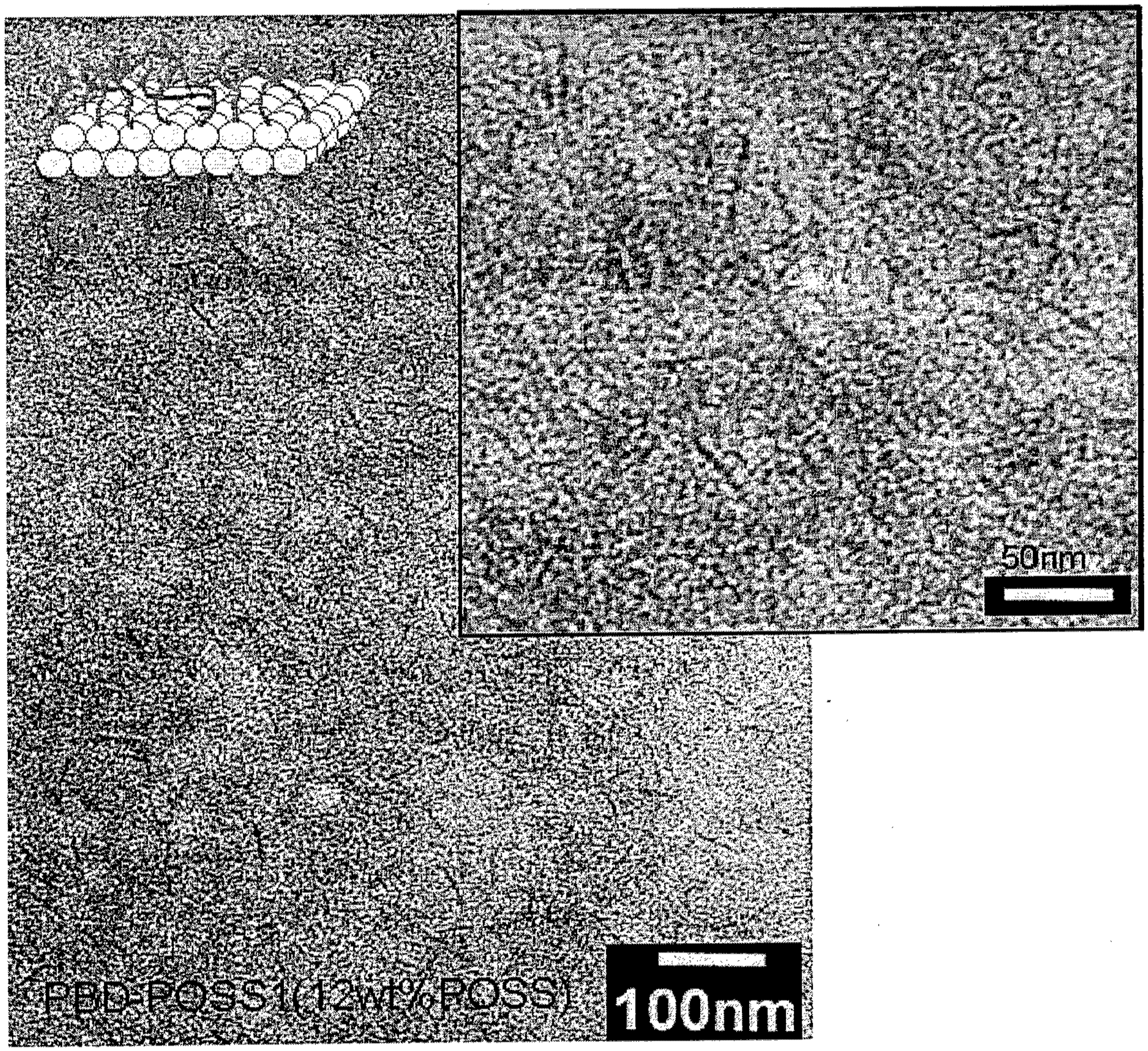


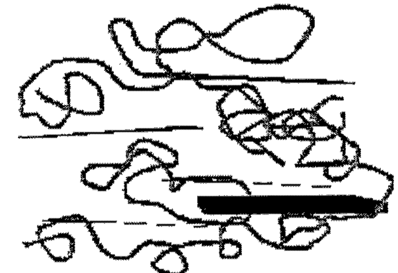
Top-down Approach



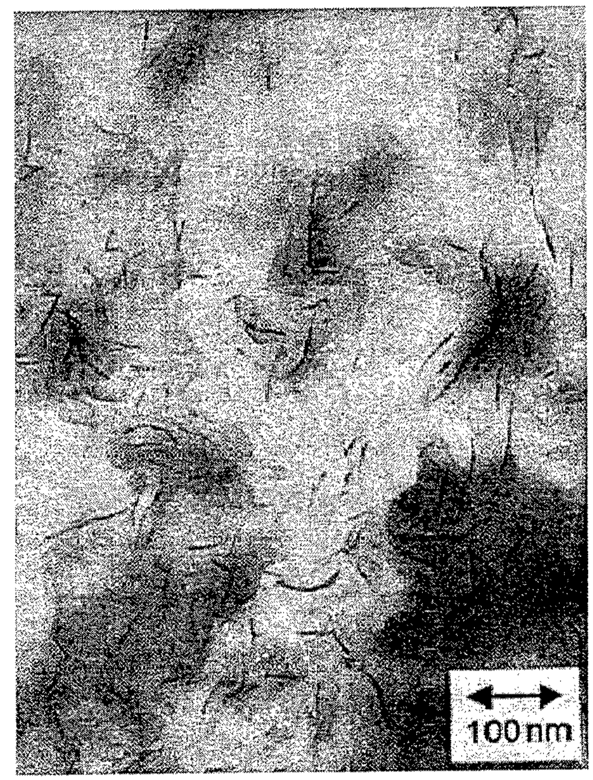
Bryan Coughlin-UMass

Coughlin Model for POSS Polymers Continued



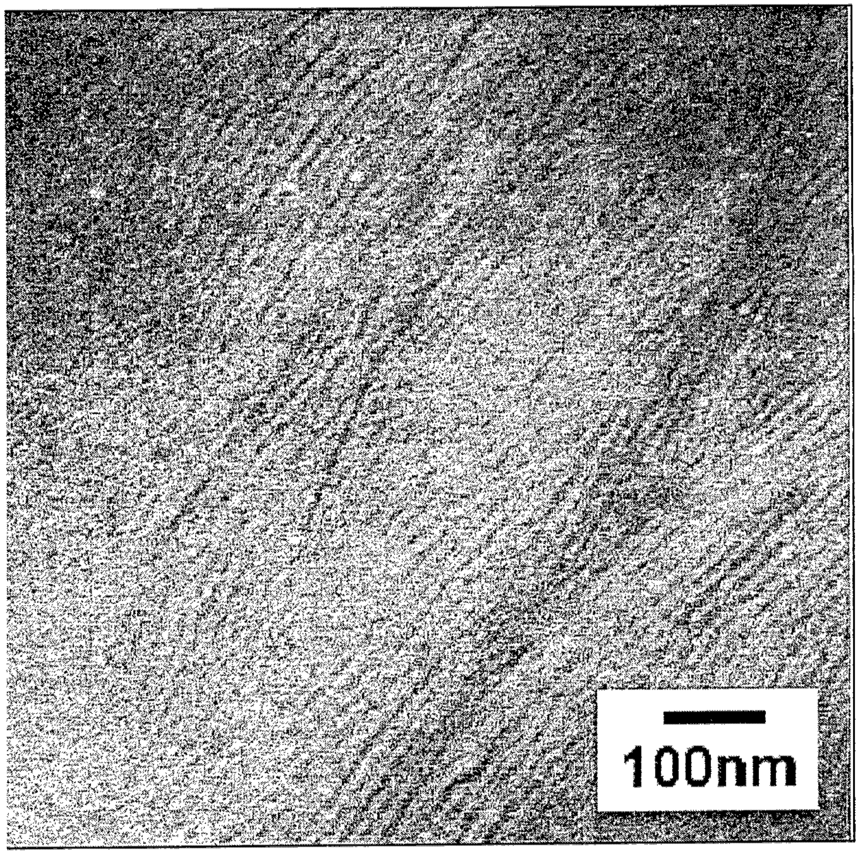


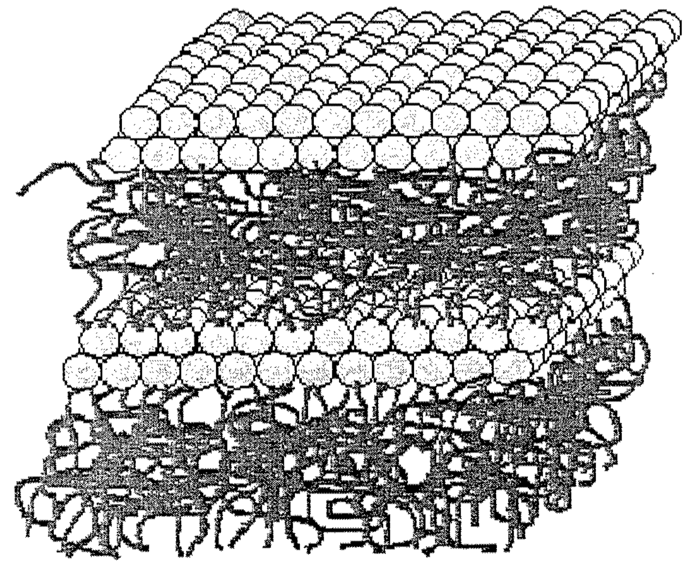
Nylon-clay



Bryan Coughlin-UMass

Coughlin Model for POSS Polymers Continued





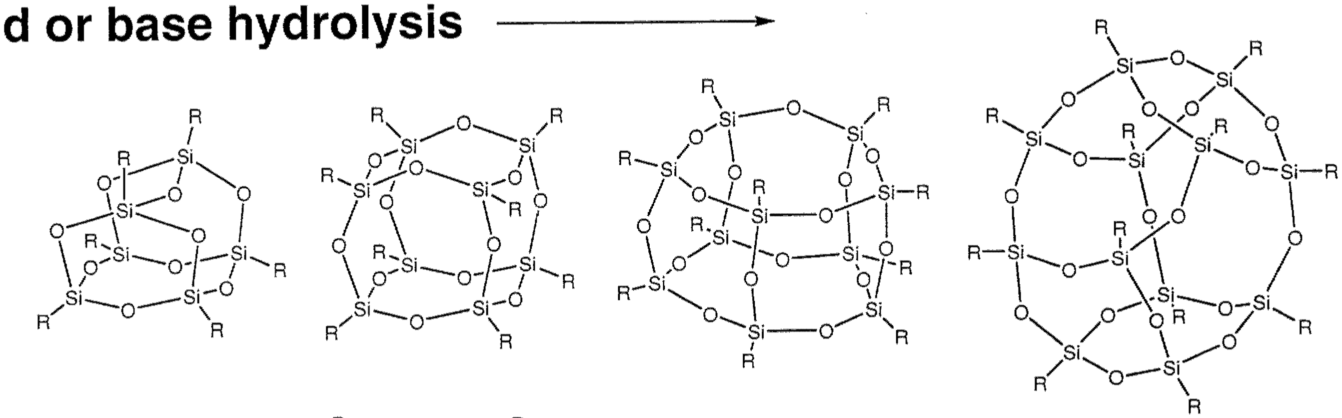
PBD-POSS4 (43wt%POSS)

Bryan Coughlin-UMass

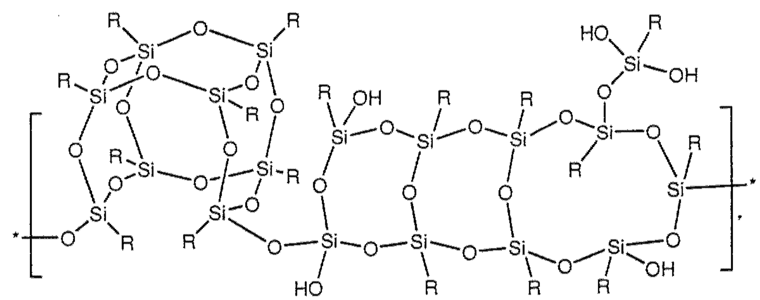
POSS Synthesis

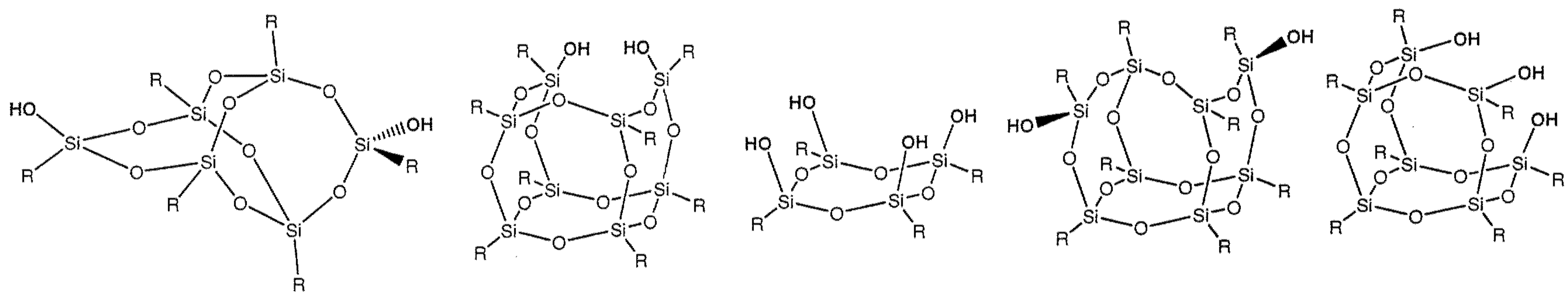
$RSiX_3$ acid or base hydrolysis

Blendables



Resin

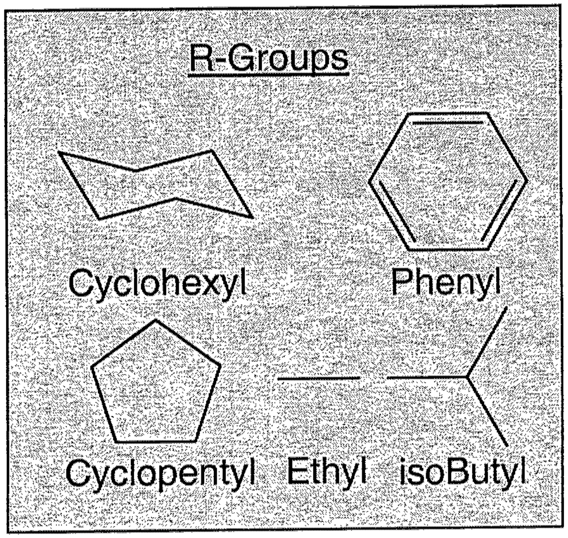




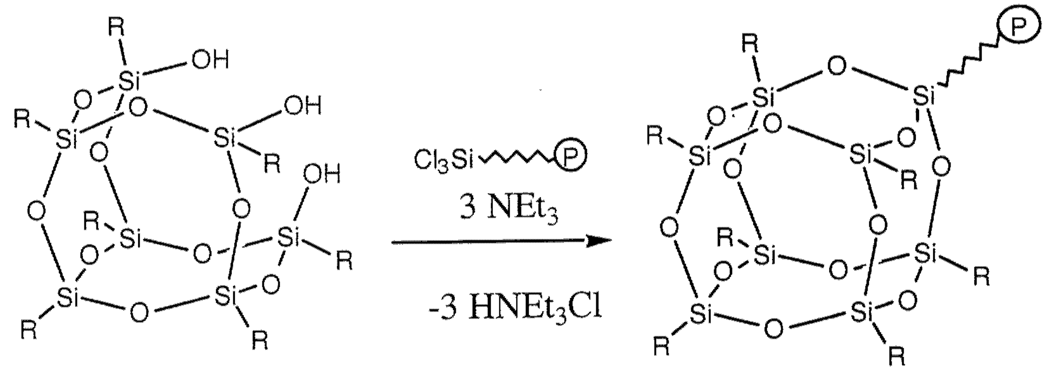
Incompletely condensed cages

Brown, Feher, AFRL, Hybrid Plastics

POSS Macromers For Nanocomposites



Completely New Polymer Feedstock Technology



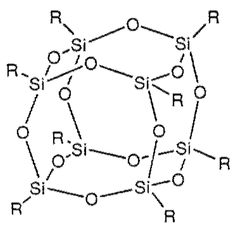
Halides	Nitriles	Silanes	Styryls
Alcohols	Amines	Silanols	a-olefins
Esters	Isocyanates	Silylchlorides	Acrylics
Bisphenols	Epoxides		Norbornenyls

POSS-based macromers are available through either **Gelest** or **Aldrich**

POSS technology is commercialized by **Hybrid Plastics** in Fountain Valley CA

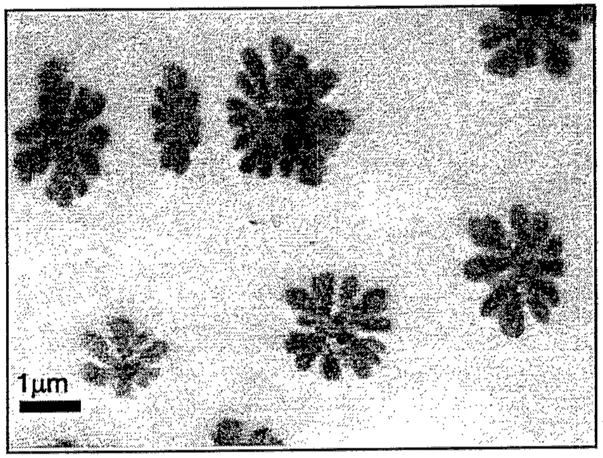
Importance of R groups: Affect compatibility with polymer matrix

50 Wt % POSS Blends in 2 Million MW PS

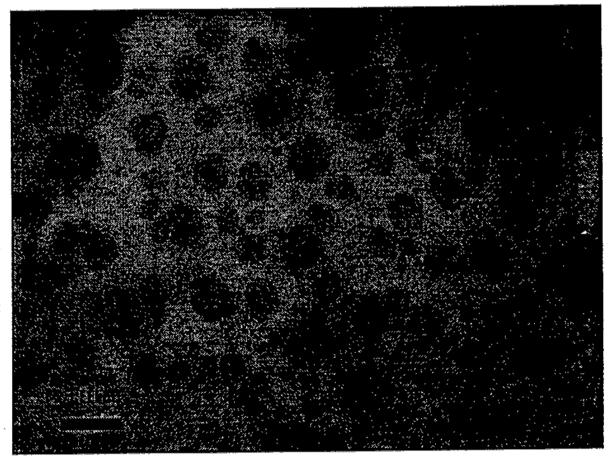


R = cyclopentyl

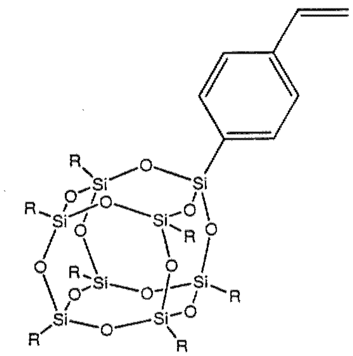
Cp_8T_8



Domain Formation

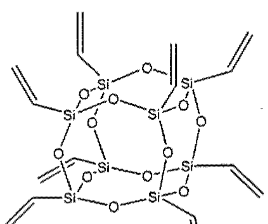


Partial Compatibility



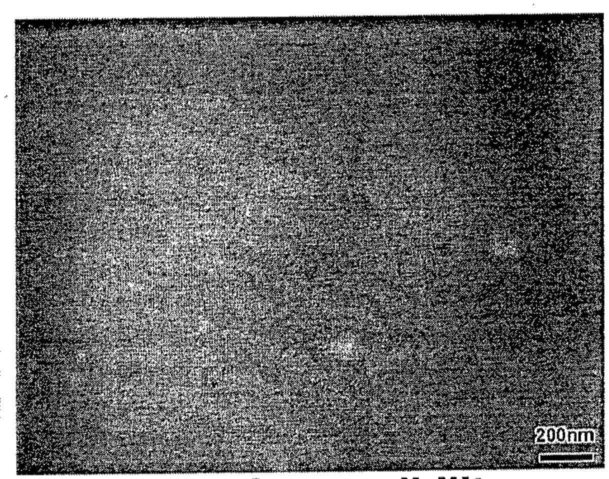
R = cyclopentyl

Cp_7T_8Styryl

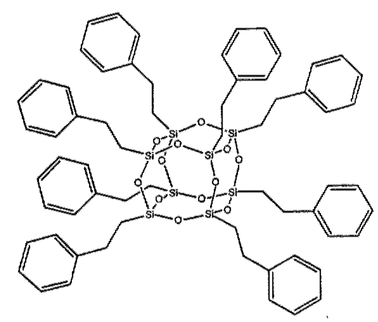


Vi_8T_8

Immiscible POSS Crystallites



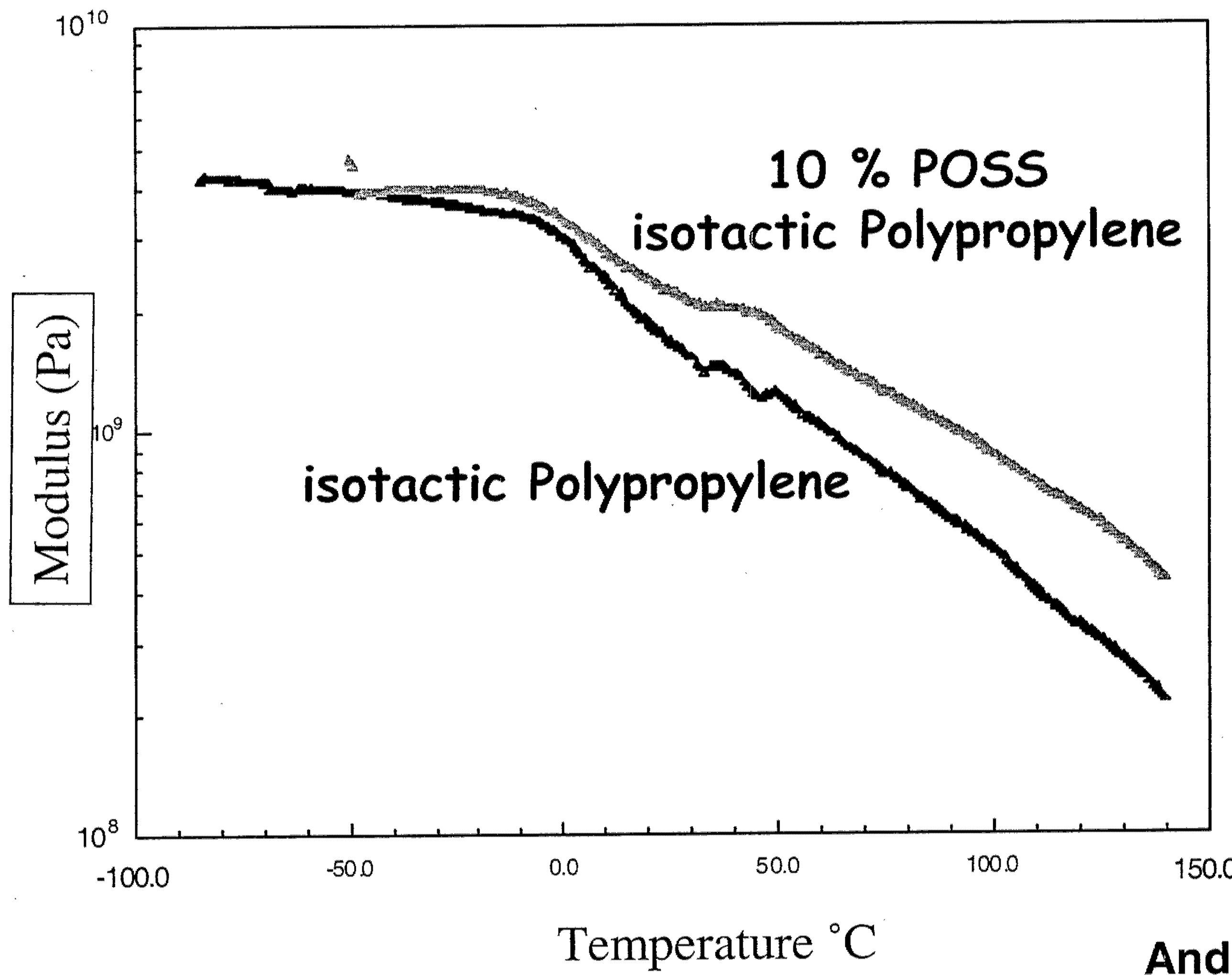
Complete Compatibility-
POSS Nanodispersion/Transparent

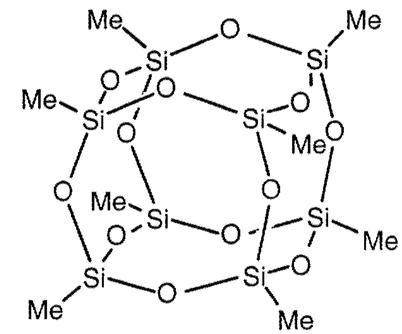


Phenethyl$_8$T$_8$

Blanski, et al., *Polymer Preprints*, **2000**. 41(1): p. 585.

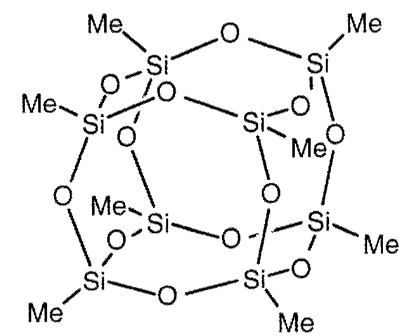
DMA of 10 Wt% POSS in isotactic Polypropylene





Polypropylene and Methyl$_8$T$_8$

POSS Drop Test
Me8T8/i-PP
Dr. R. Blanski,
AFRL
Test Duration:
15:01
Time Lapse 20X
8 Feb 2001



- Test run at 190 °C
- 1 Kg weight
- 10% POSS gave a 28 % improvement

POSS Polypropylene Blends

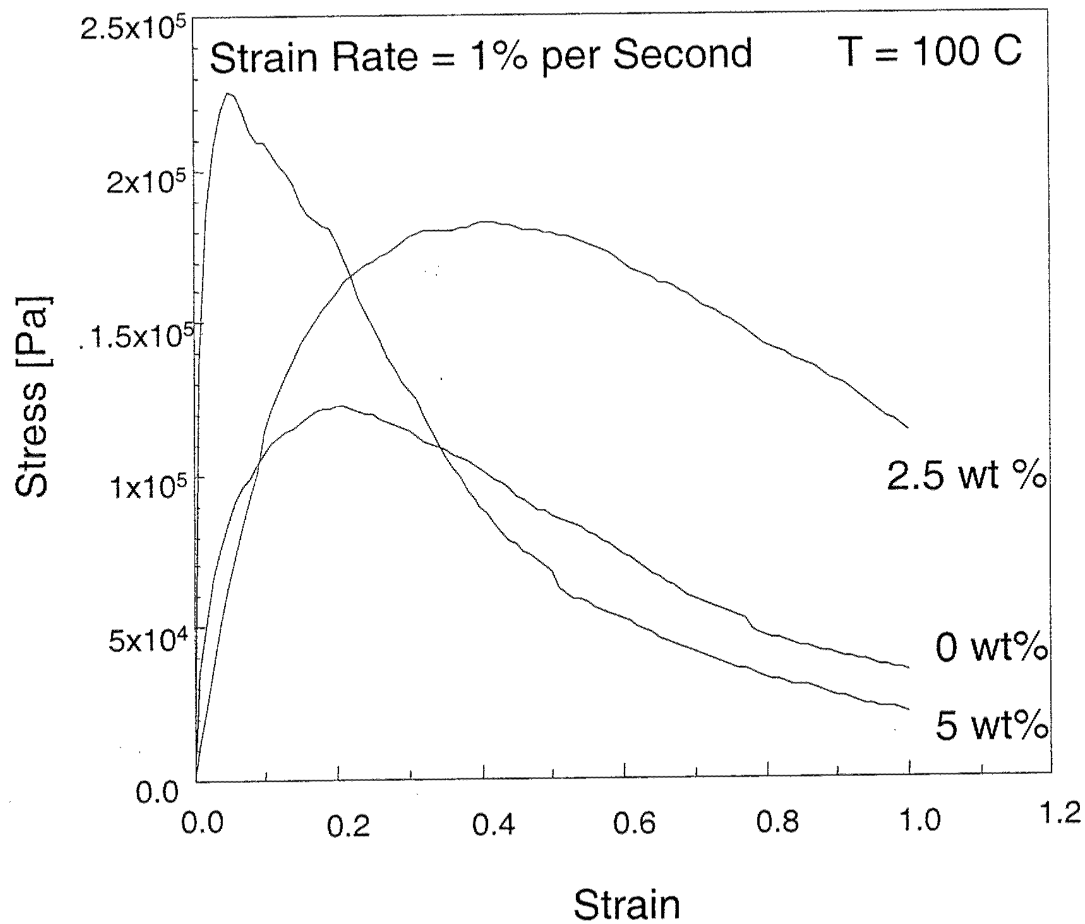
	Dow data	Neat *i*-PP (processed)	*i*-PP blended 2 wt% $Methyl_8T_8$	*i*-PP blended 5 wt% $Methyl_8T_8$	*i*-PP blended 10 wt% $Methyl_8T_8$
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min, 1% secant); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

- **The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.**

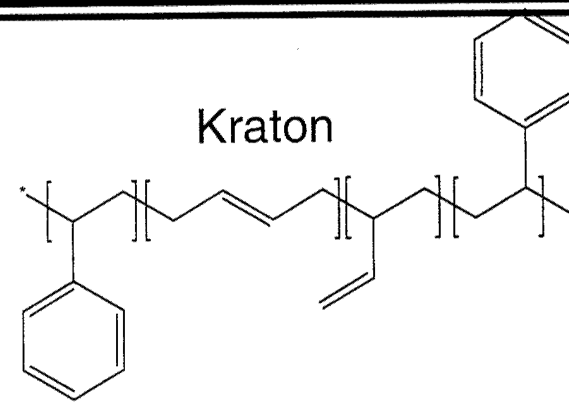
Andre Lee

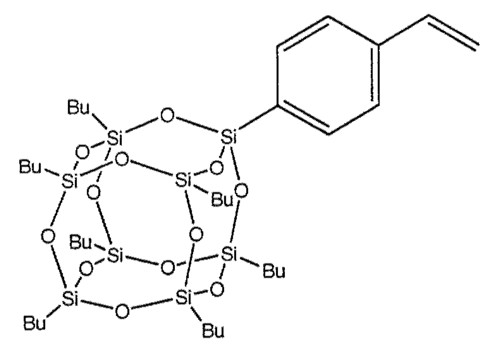
POSS Kraton Blends

Kraton-iButyl$_7$T$_8$StyrylPOSS



Kraton





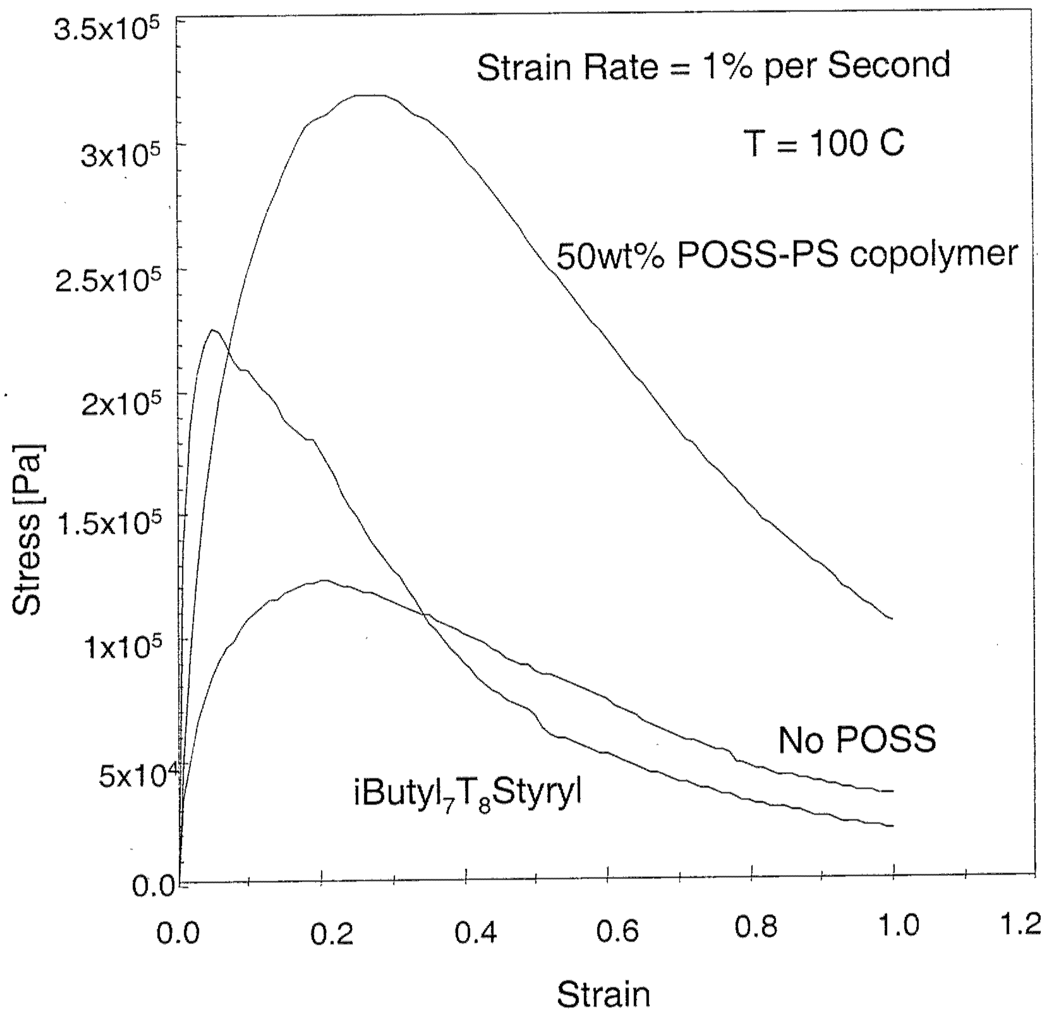
iButyl$_7$T$_8$Styryl

2.5 wt% POSS nearly doubles toughness!

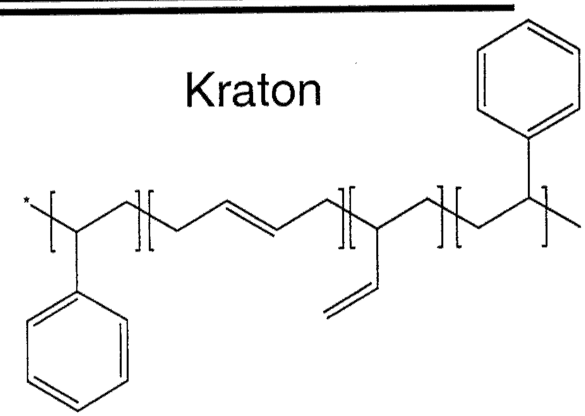
Andre Lee, AFRL

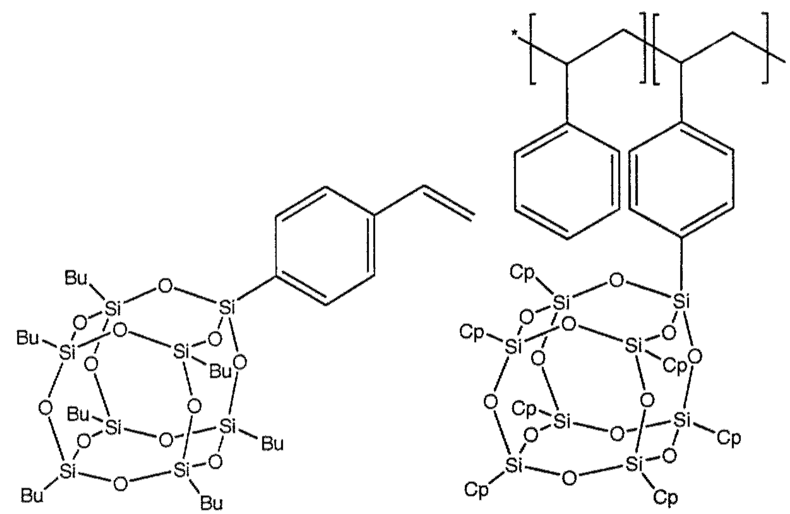
POSS Kraton Blends

Kraton-5%wt POSS



Kraton





iButyl$_7$T$_8$Styryl

50wt% POSS-PS copolymer

Andre Lee, AFRL

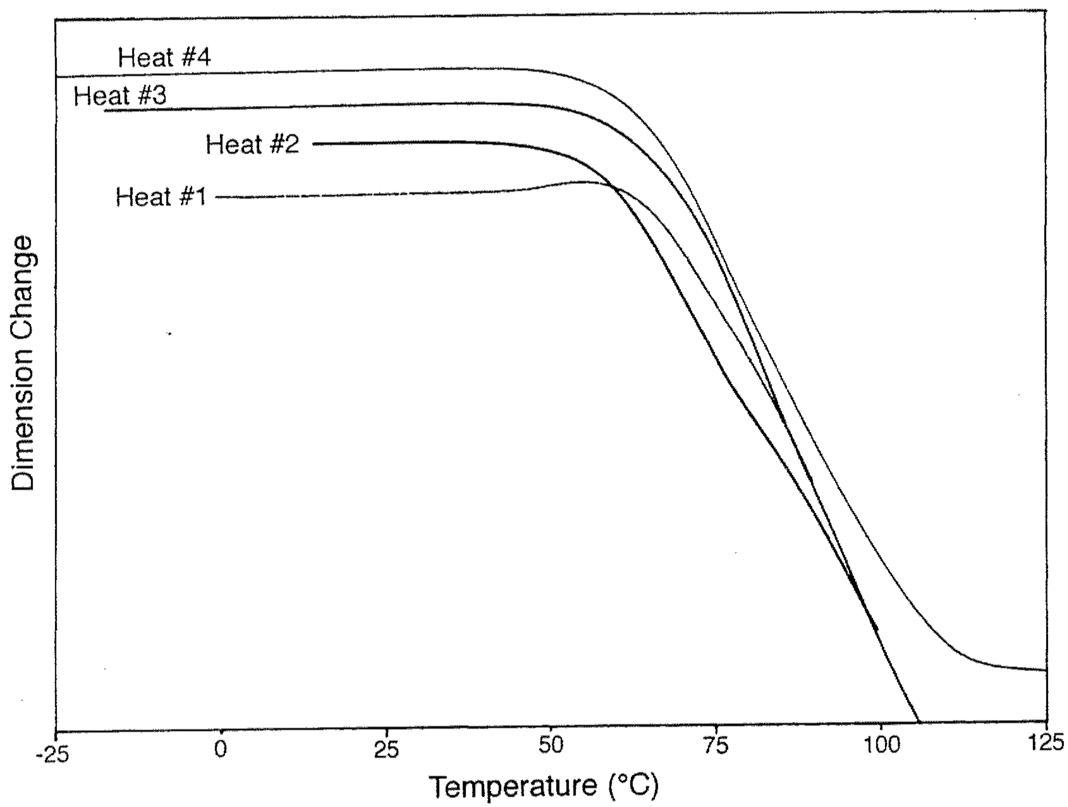
POSS Blends with Semi-Crystalline Thermoplastics

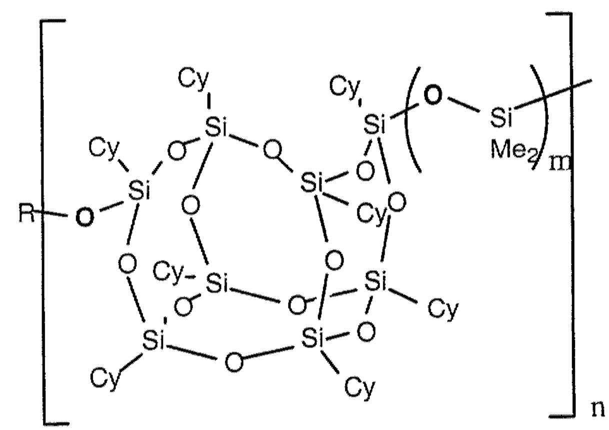
- POSS R-group determines compatibility
- POSS copolymers can also blend
- POSS improves thermomechanical properties
  - 25 °C improvements in HDT with just 10 wt % POSS
  - A doubling or better of toughness using 2.5 wt % POSS
- Processing / mixing methods are critical

POSS Bead & Pendent Siloxanes

POSS PDMS TMA Characterization

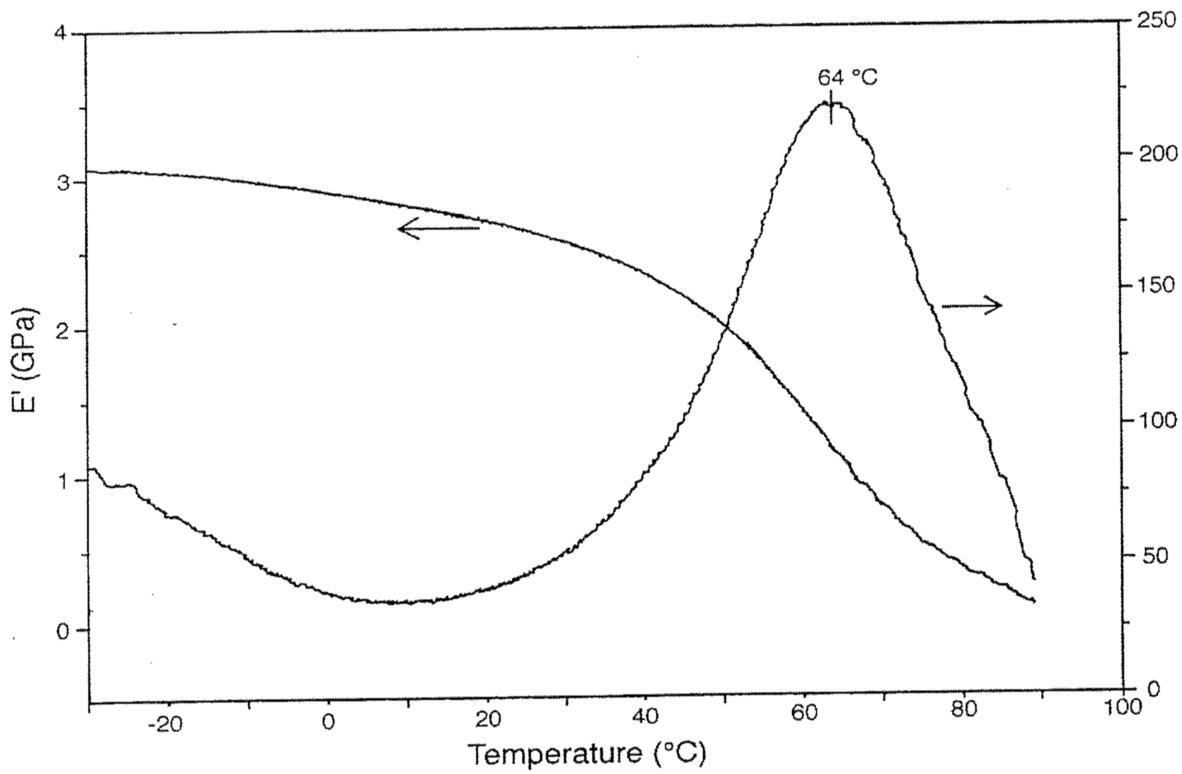
The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.

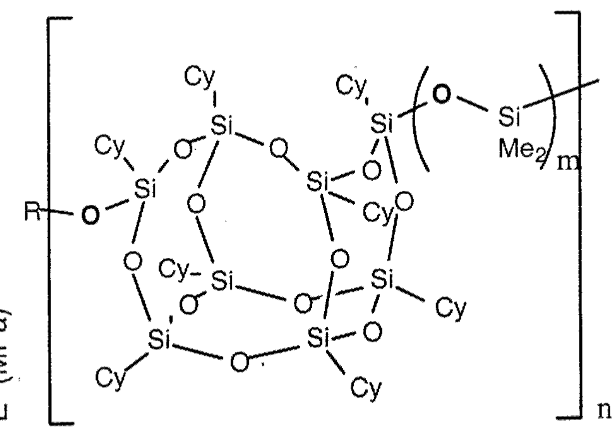




DMA Characterization

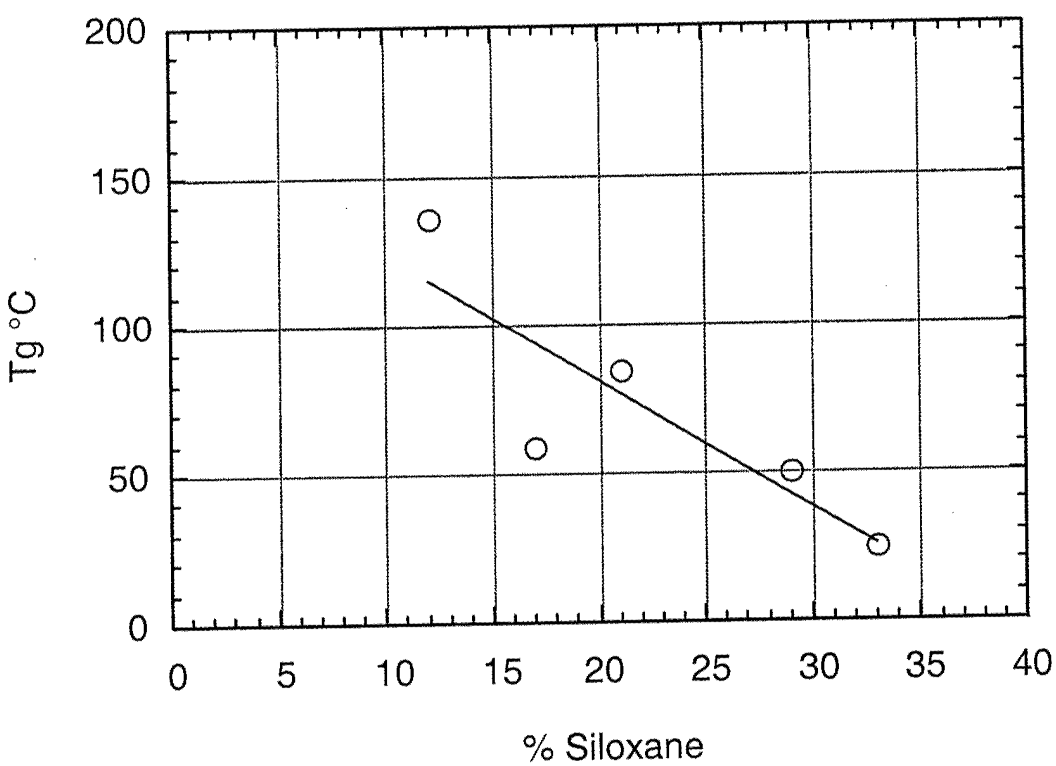
The copolymers with low softening temperatures can also be molded into bars for mechanical testing. Dynamic mechanical analysis reveals a T_g (64°C) and the tail end of a sub T_g relaxation (-20°C).

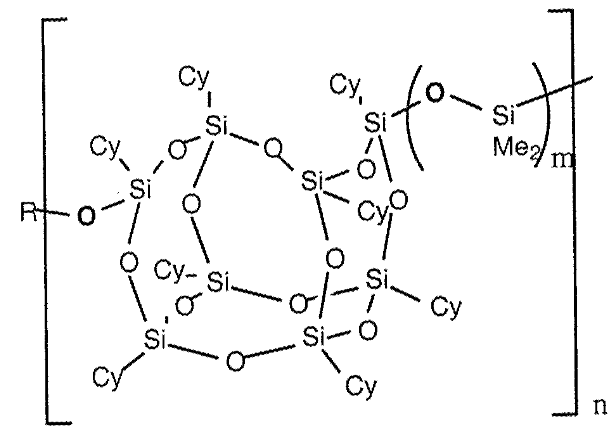




Tg's For Bead Siloxane Copolymers

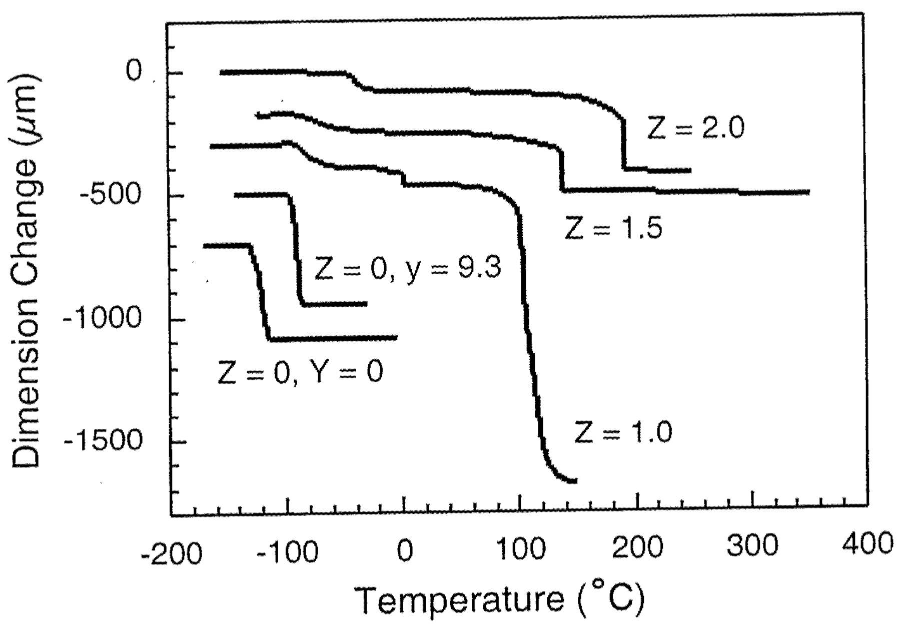
Glass Transition vs % Siloxane

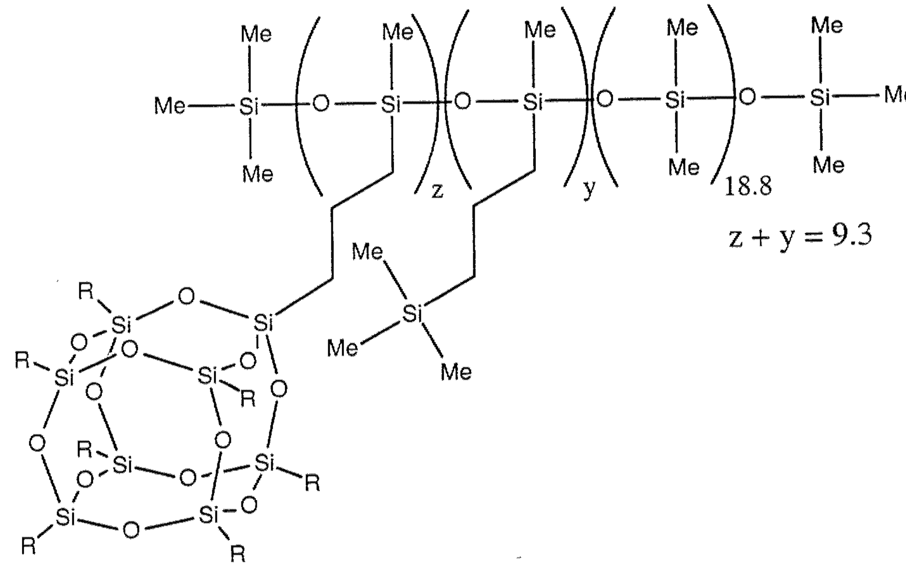




POSS Bead acts as a hard segment

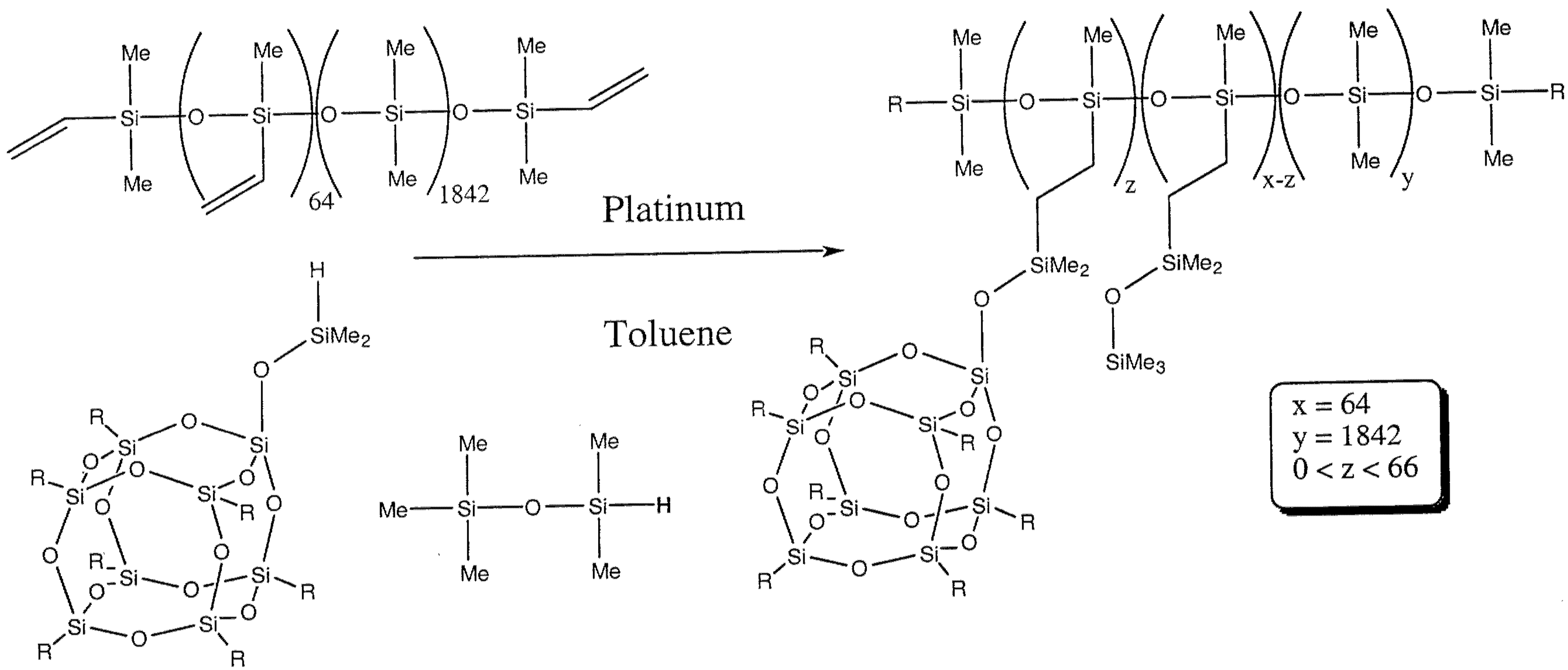
TMA of Pendent POSS Siloxanes





$z + y = 9.3$

Hydrosilation to High MW PDMS



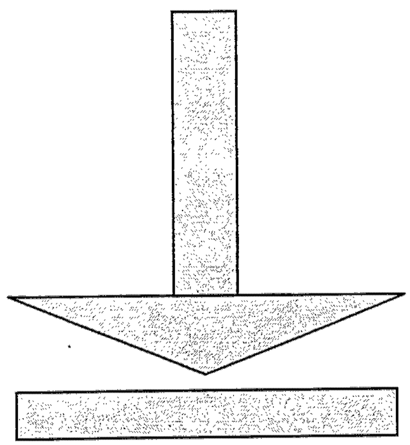
Used 5 weight % POSS

There are about 7 POSS-macromers per PDMS chain

Experimental Setup for Rheology

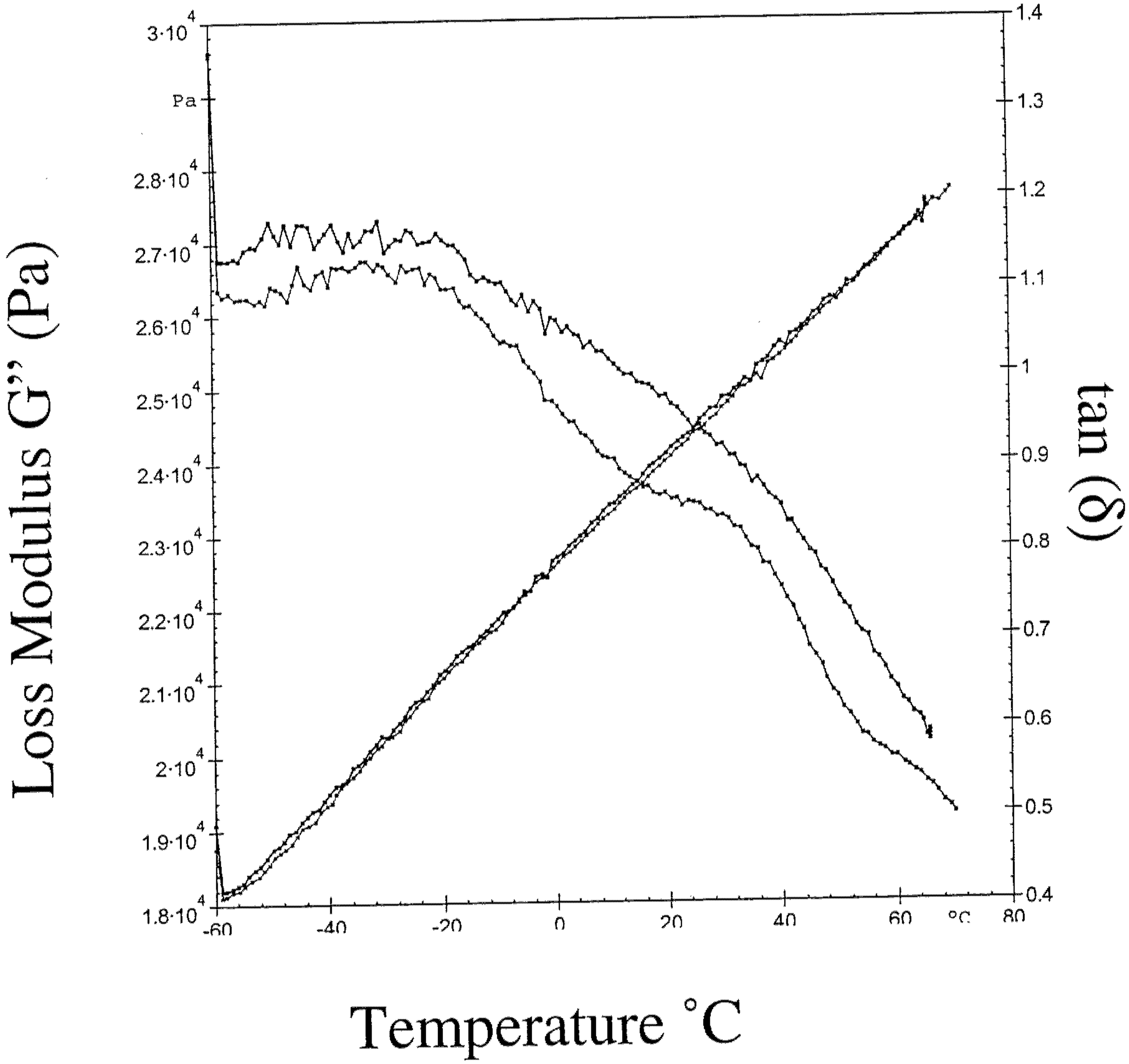
$$\gamma(\omega)=\gamma_o \sin(\omega t)$$

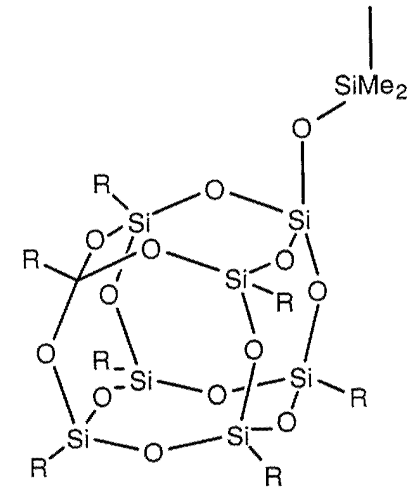
$$\omega=2\pi \ (\mathrm{sec}^{-1})$$



- 25 mm diameter cone-and plate with cone angle of 2° was used.
- The strain amplitude γ_o is 1% and angular frequency ω is 2π per second.
- The temperature is ramped from -60°C to 70°C with a rate of 2°C/min.
- The loss modulus G" and $\tan\delta$=G"/G' were obtained as a function of temperature.

Effect of 5 wt % Cyclopentyl POSS

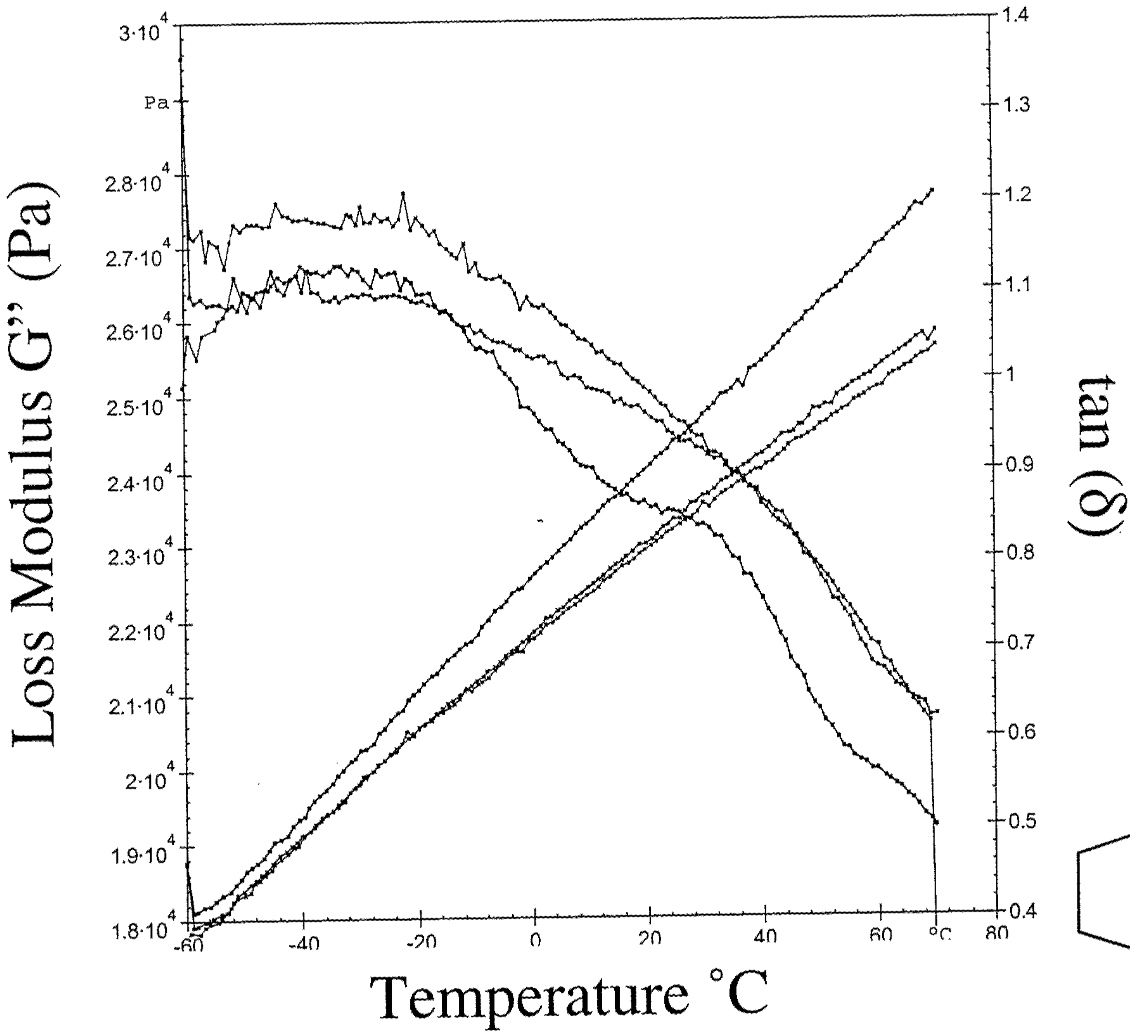




Red = PDMS + 5 wt% cyclopentylPOSS
Blue = PDMS + Pt

Andre Lee, AFRL

Comparison of Three T8-POSS Macromers

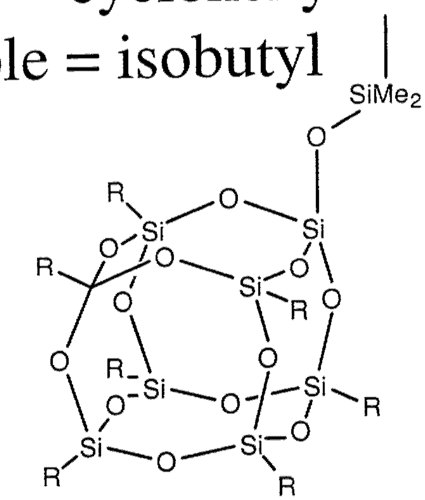


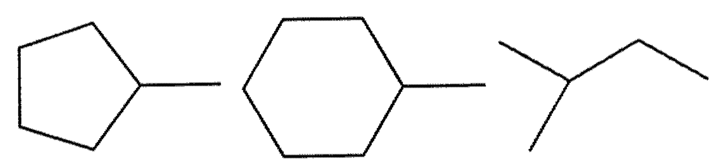
PDMS + 5 wt % POSS

Blue = cyclopentyl

Red = cyclohexyl

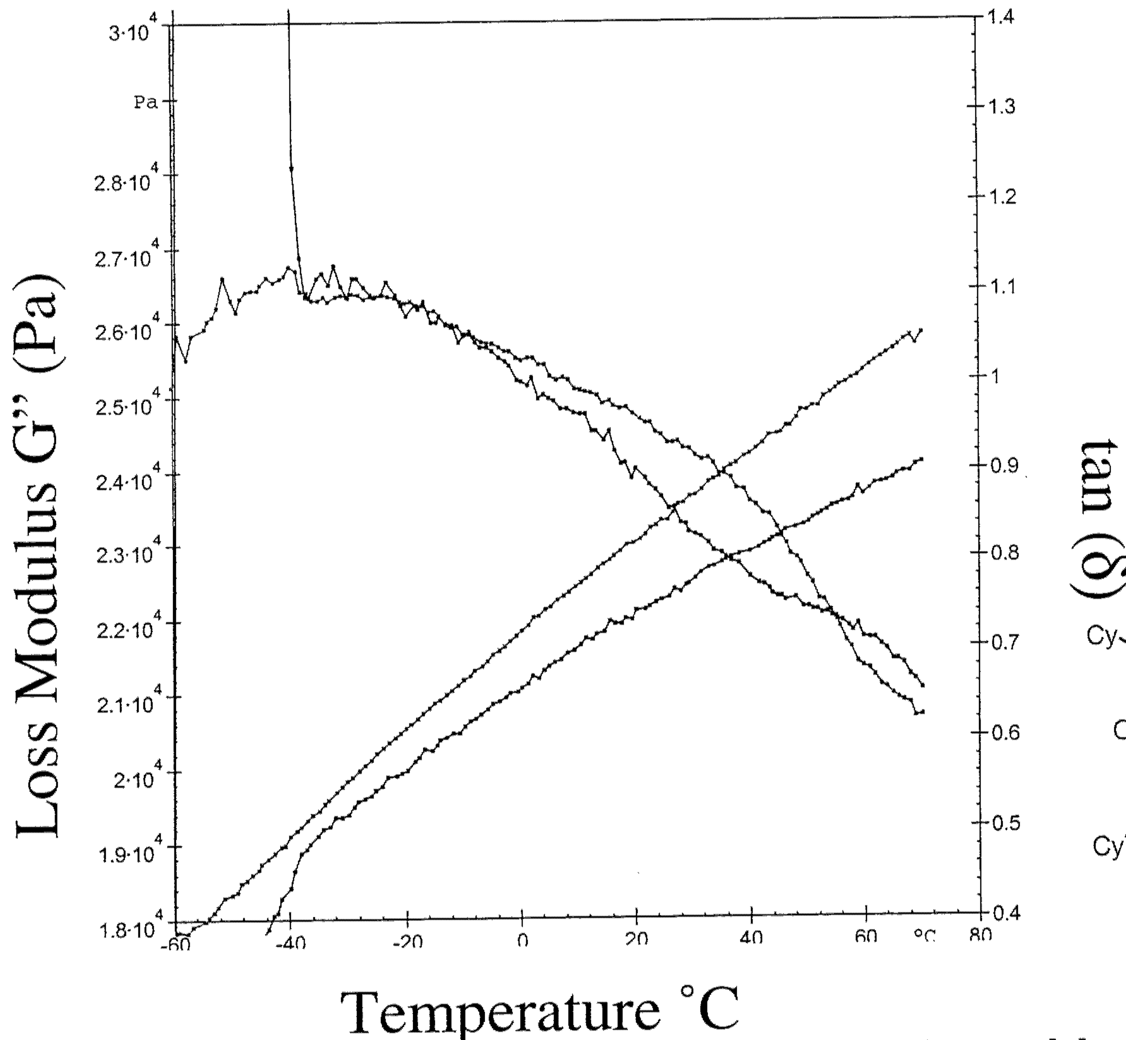
Purple = isobutyl





Andre Lee, AFRL

Comparison of Two POSS Polyhedra

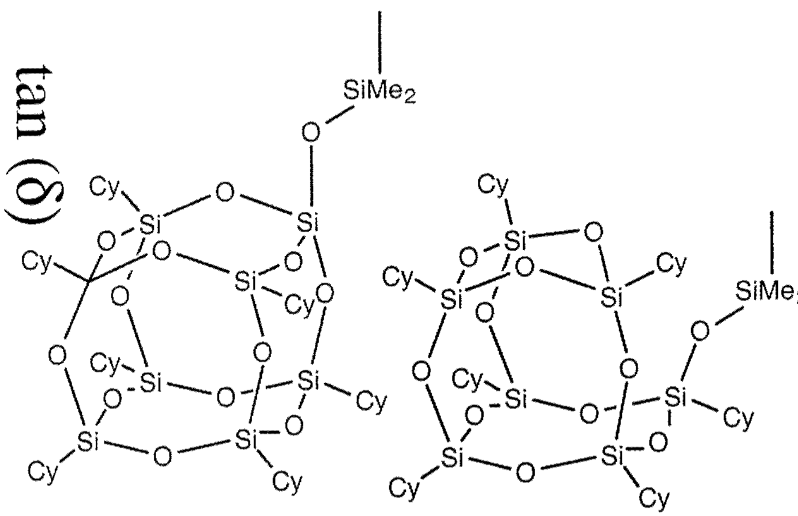


PDMS + 5 wt %

CyclohexylPOSS

Red = T8-POSS

Blue = T7-POSS



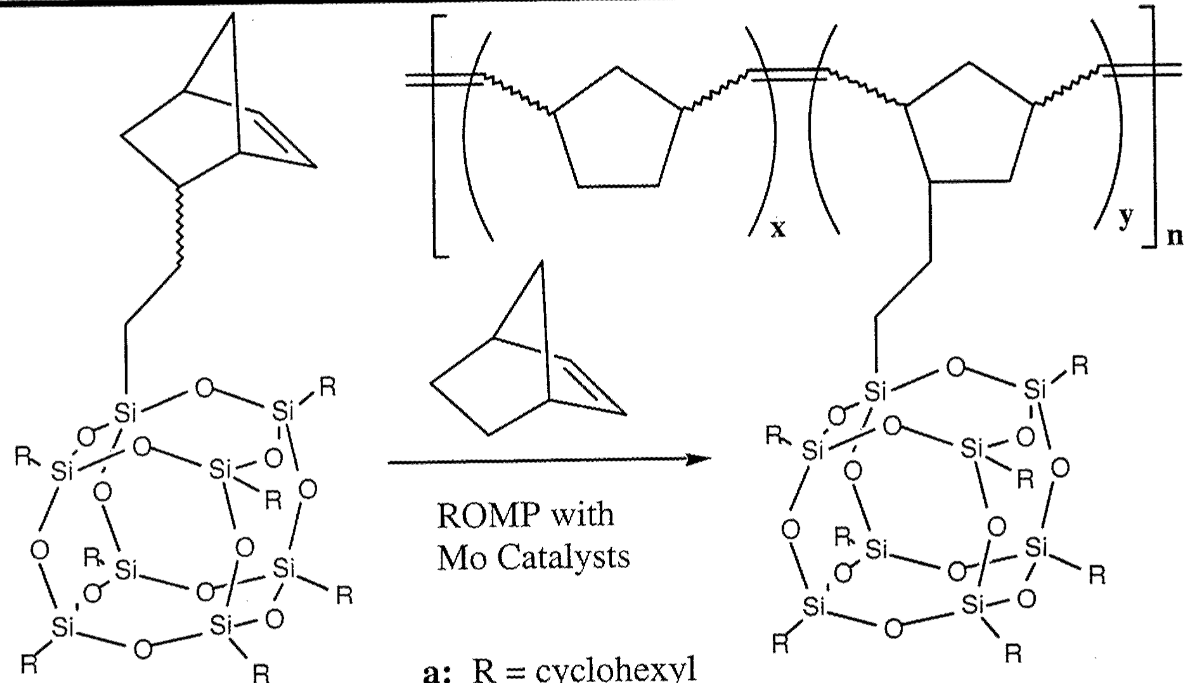
Continue this collaboration with Andre Lee

POSS Siloxane Copolymers

- A pendent POSS is more effective than a bead POSS
  - For bead siloxanes, POSS acts as a hard segment; 75 wt % POSS raises the T_g almost 200°C.
  - For pendent siloxanes, 30 wt% POSS raises the T_g over 200°C.
- Rheology of 5 wt% POSS High Mw PDMS demonstrates the effect of R-group <u>solubility</u> and POSS <u>cage shape</u> on POSS-polymer interaction.

POSS Pendent Rubbery Polymers

Polymerization of POSS Norbornenes



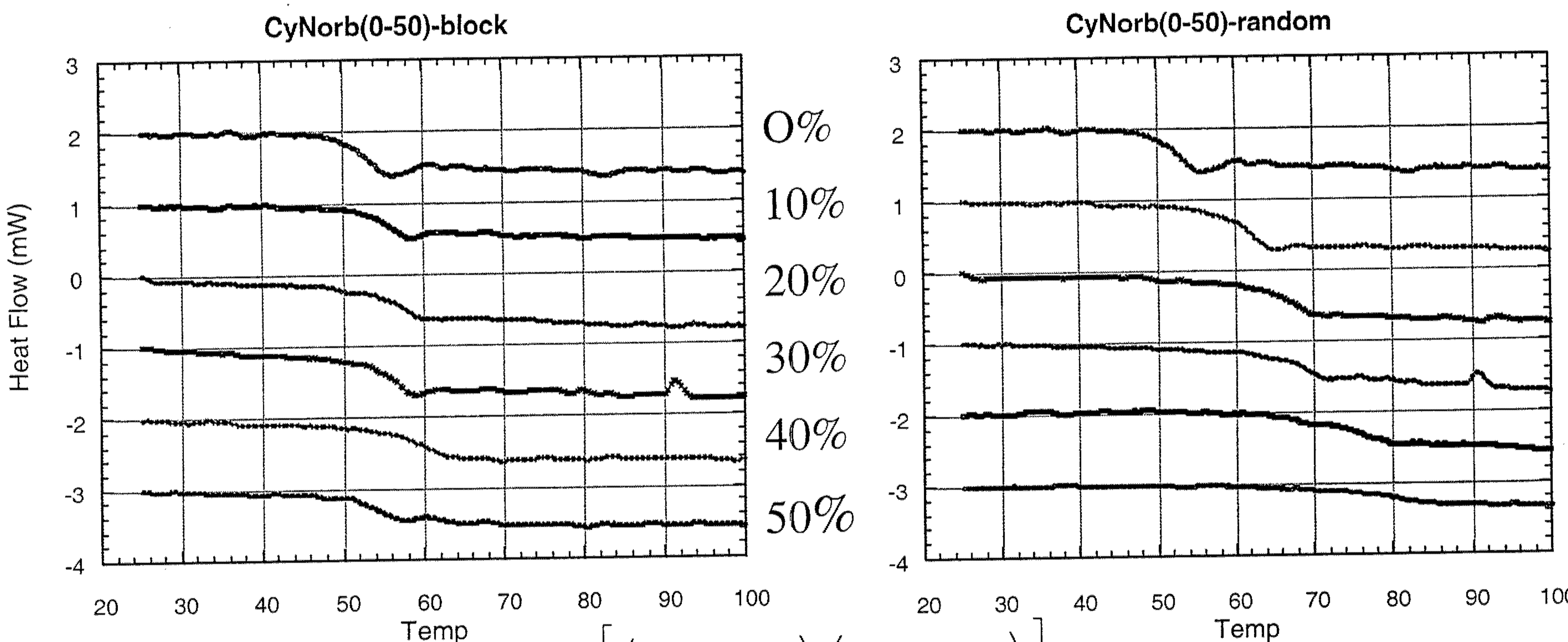
6a,b

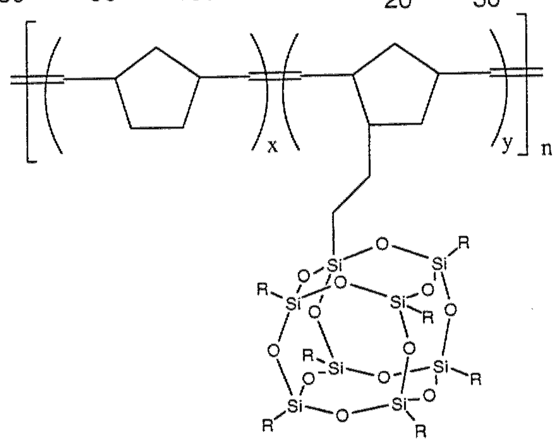
a: R = cyclohexyl
b: R = cyclopentyl

7a,b

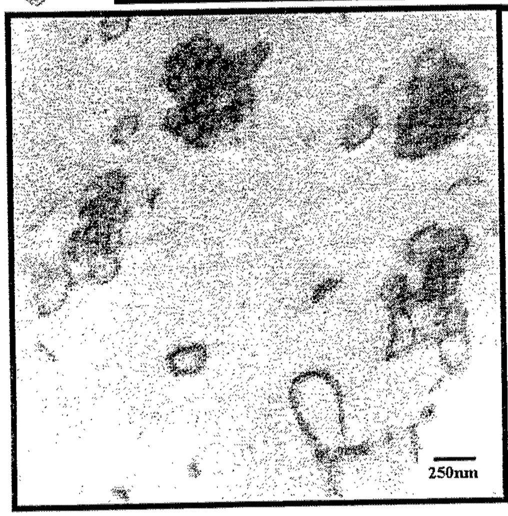
Both block and random copolymers were synthesized.
The wt. % POSS was varied from 0 to 50 wt. % POSS.

DSC Data for POSS Norbornenes



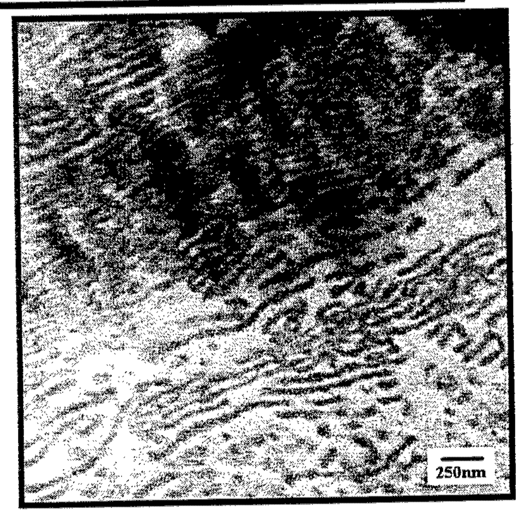


TEM of Diblock POSS Norbornenes

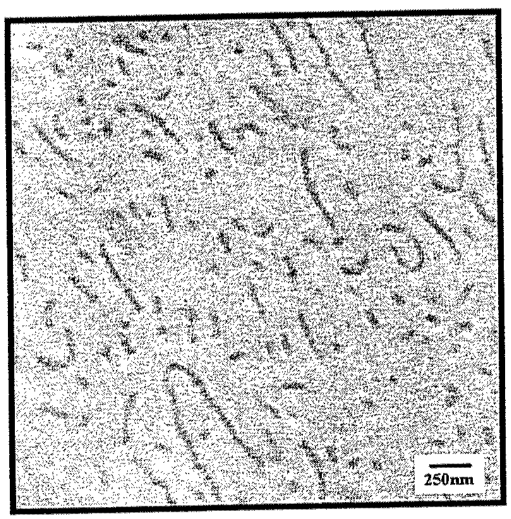


10wt % of CpPOSS

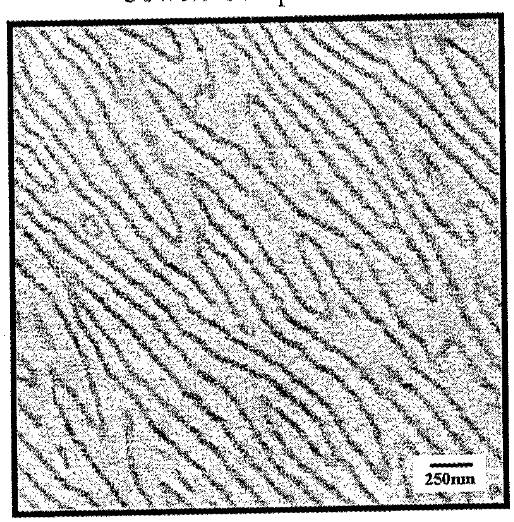
30wt% of CpPOSS



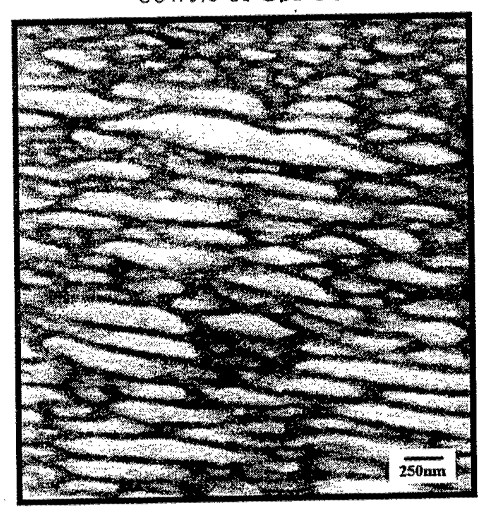
60wt% of CpPOSS



10wt% of CyPOSS



30wt % of CyPOSS

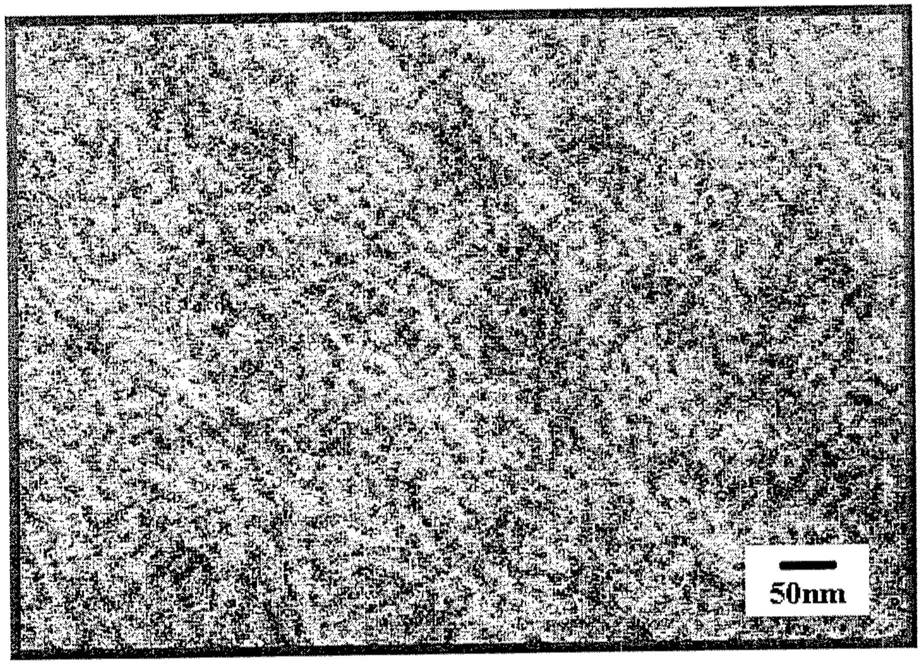


60wt% of CyPOSS

Pat Mather, AFRL

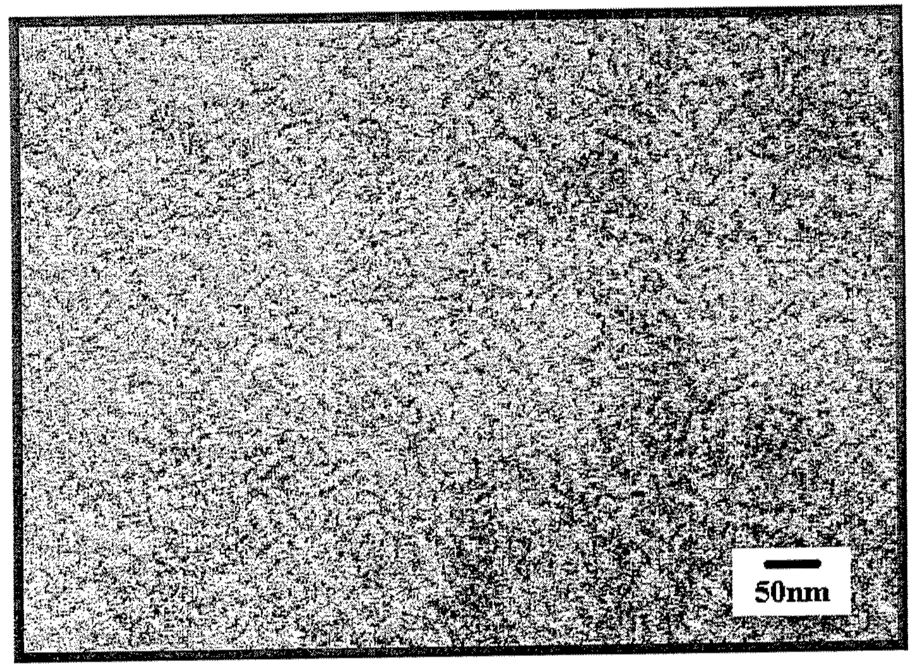
TEM of Random POSS Norbornenes

50CyPOSS/PN



"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

50CpPOSS/PN

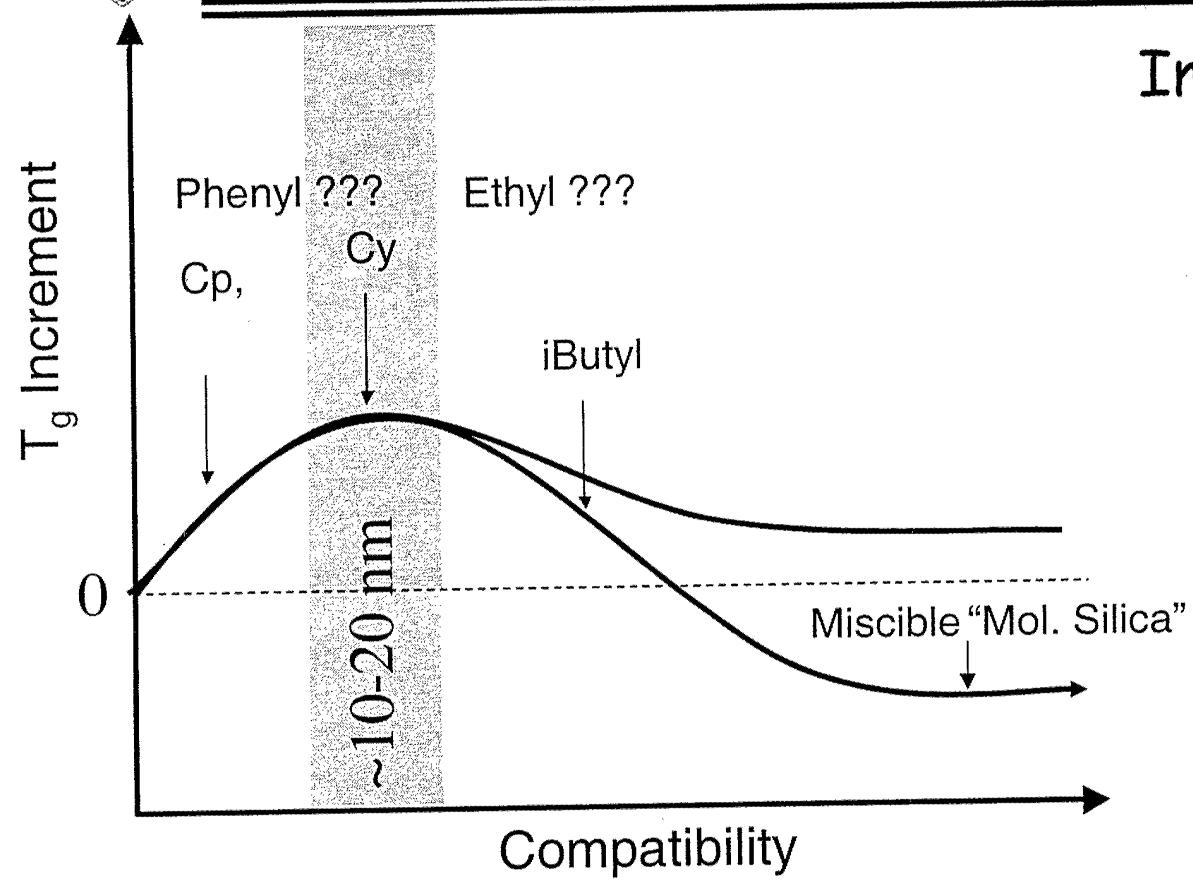


"Fine" Cylinder Nanodstructure
(Diameter ~ 6nm)

Cyclohexyl POSS-rich domains may entrain more unoriented polynorbornene chains than Cyclopentyl POSS-rich domains.

Pat Mather, AFRL

Mather/Haddad Model for POSS Polymers



Importance of R!

POSS-norbornyl and POSS-PS random copolymers

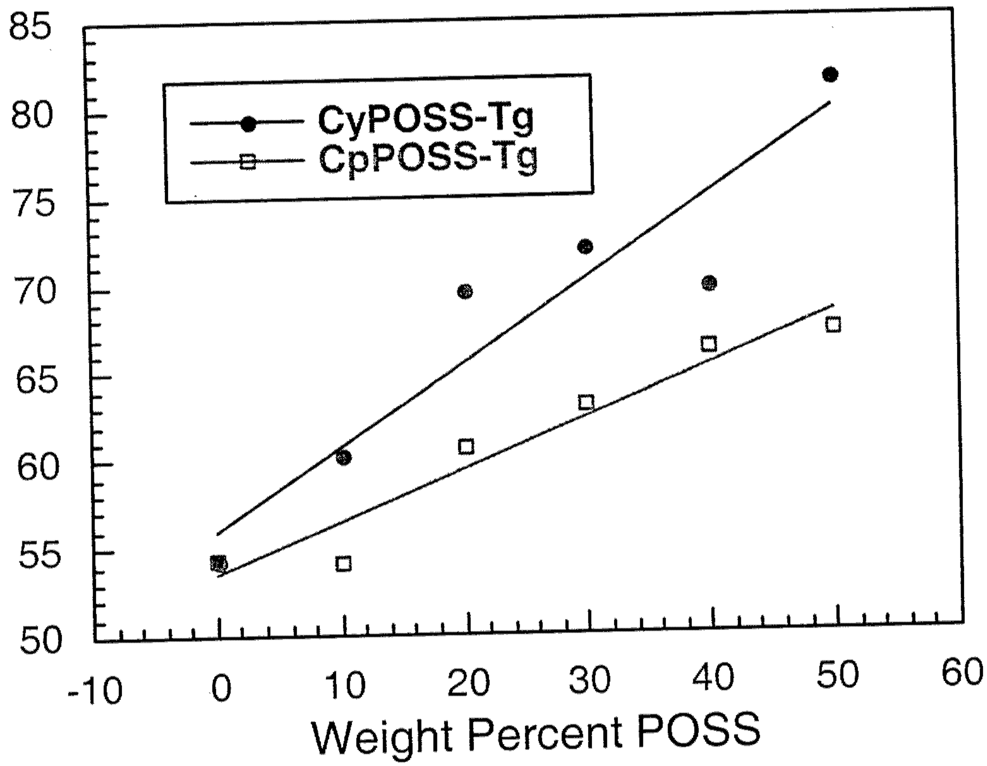
-significant sensitivity of thermomechanical properties to R = Cy and Cp

- morphological analyses reveals strong correlation to the nature of aggregation

This suggests an optimized (yet unknown) length-scale of aggregation and aggregation nature for property improvements related to the level of compatibility between the POSS group and the host matrix.

Pat Mather, AFRL

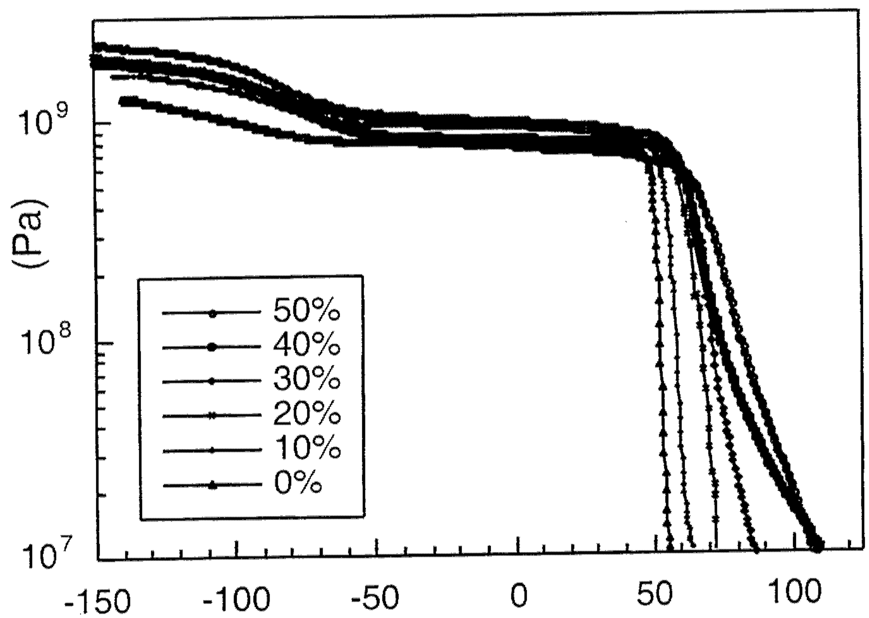
Glass Transition Temperature Variation

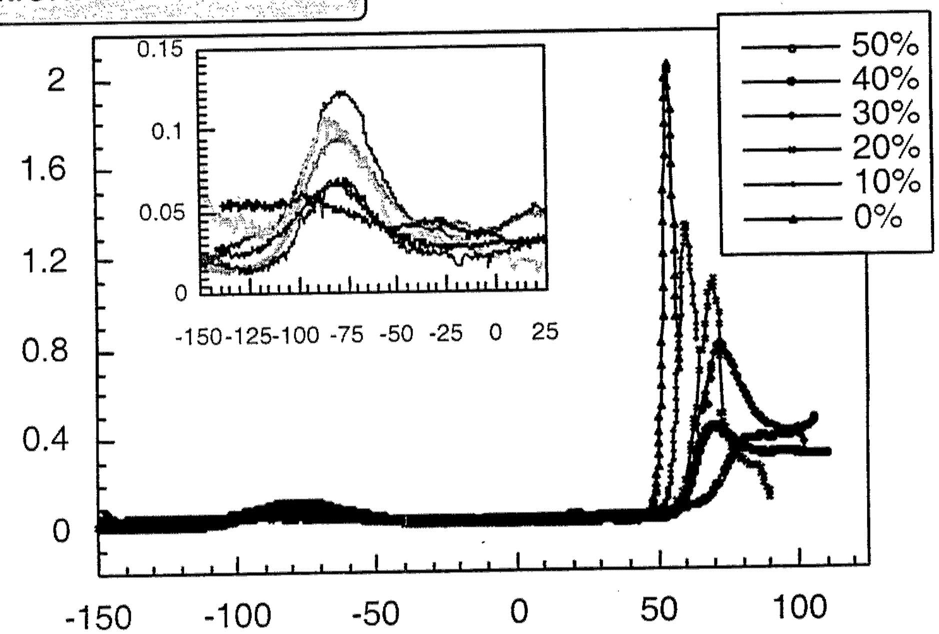


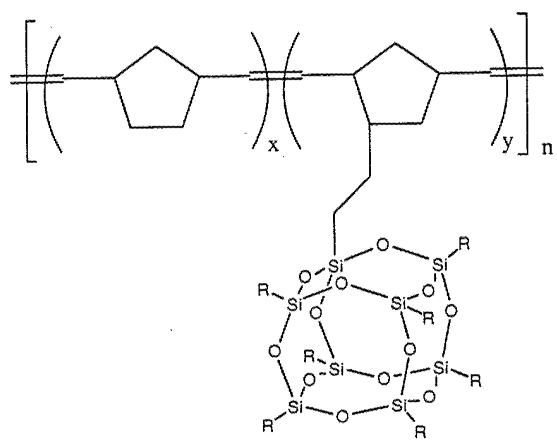
The random copolymers with CyPOSS show a larger increase in the glass transition than do their CpPOSS analogs. This subtle difference demonstrates that a small change to the nanoscale POSS filler can have a profound effect on polymer chain dynamics.

Storage Modulus and Loss Tangent

Cyclohexyl Relaxation: 14.7 kcal/mol





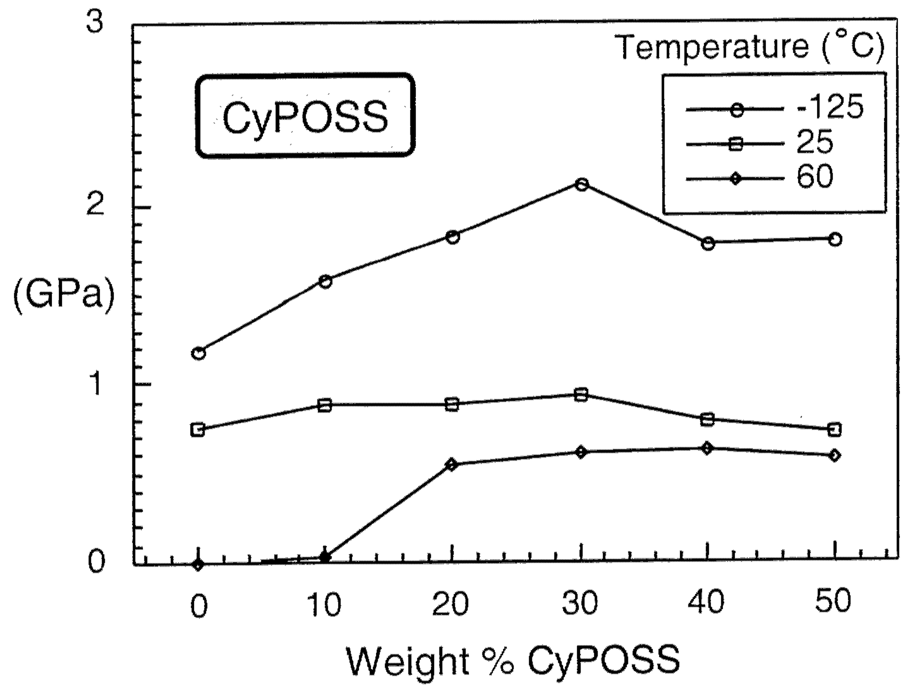


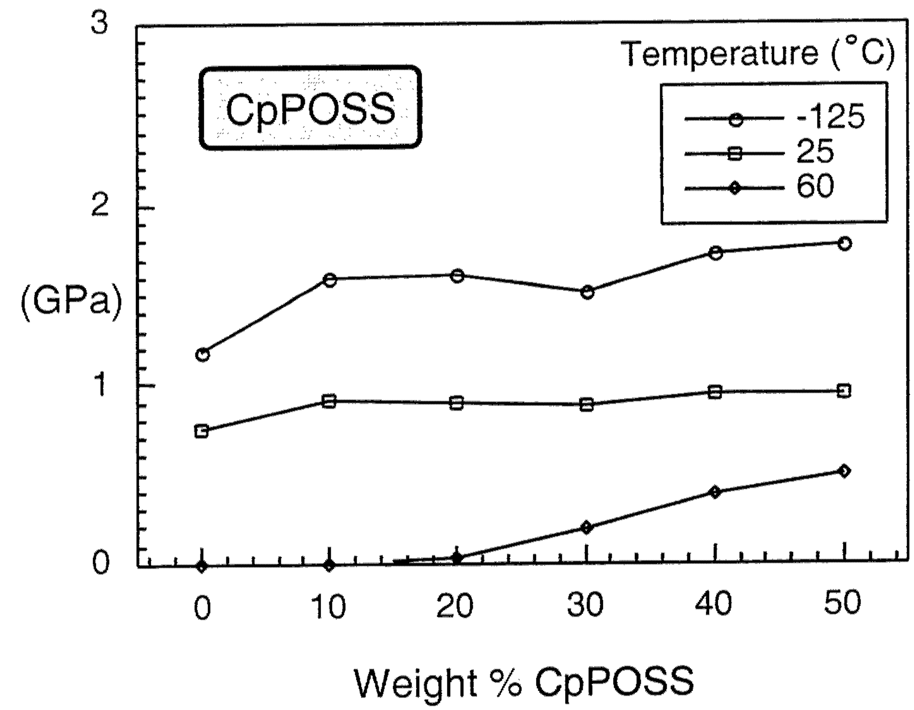
No Maximum for 50% CyPOSS

Various Wt % Cyclohexyl POSS Polynorbornene Random Copolymers

Pat Mather, AFRL

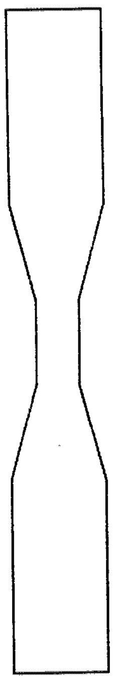
Tensile Storage Modulus Variation with POSS Content at Three Temperatures





Pat Mather, AFRL

Fracture Surface After Uniaxial Tensile Testing



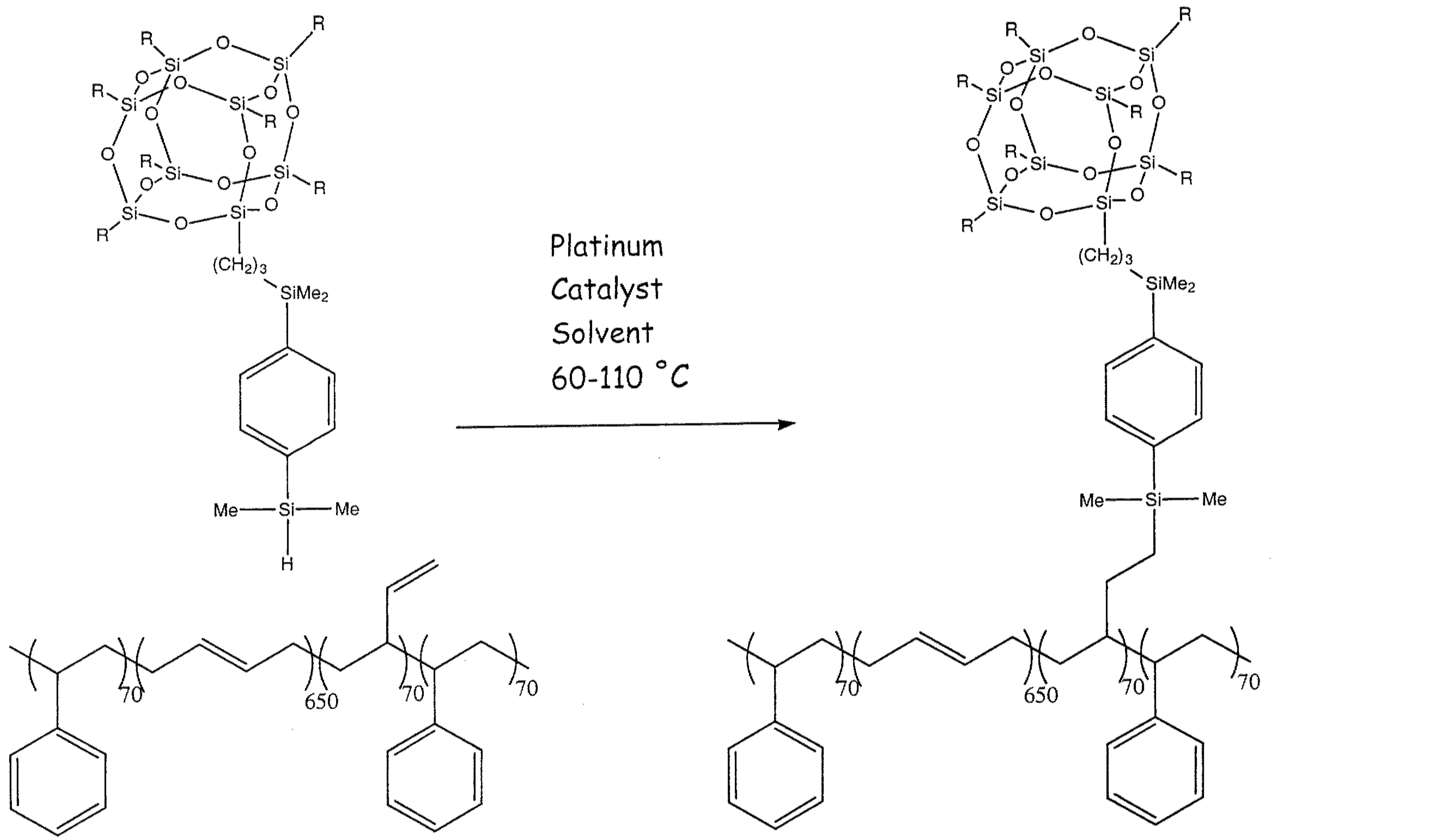
Zero Wt % POSS

10 Wt % POSS

The failure mechanism appears to be different.

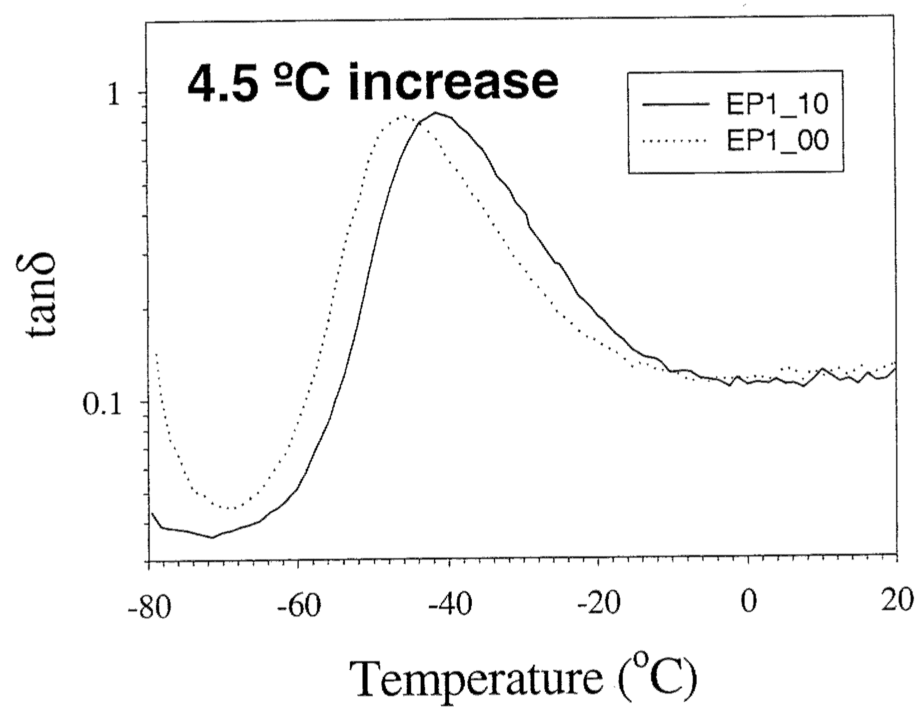
Continue this collaboration with Pat Mather

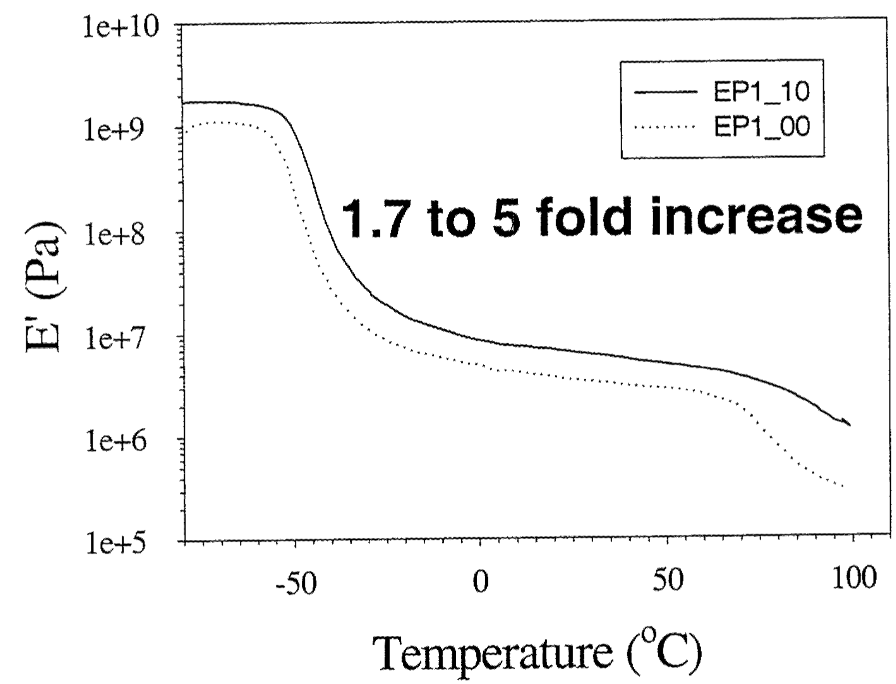
TPE POSS Kraton Grafts



- A new more reactive POSS-hydride developed for hydrosilation
- Comparison of Grafted POSS to PB vs blends of POSS to PS or PB

Ben Hsaio: POSS EP Elastomers





EP 10% Me_8T_8 Blend
Increase in Modulus and Tg Observed

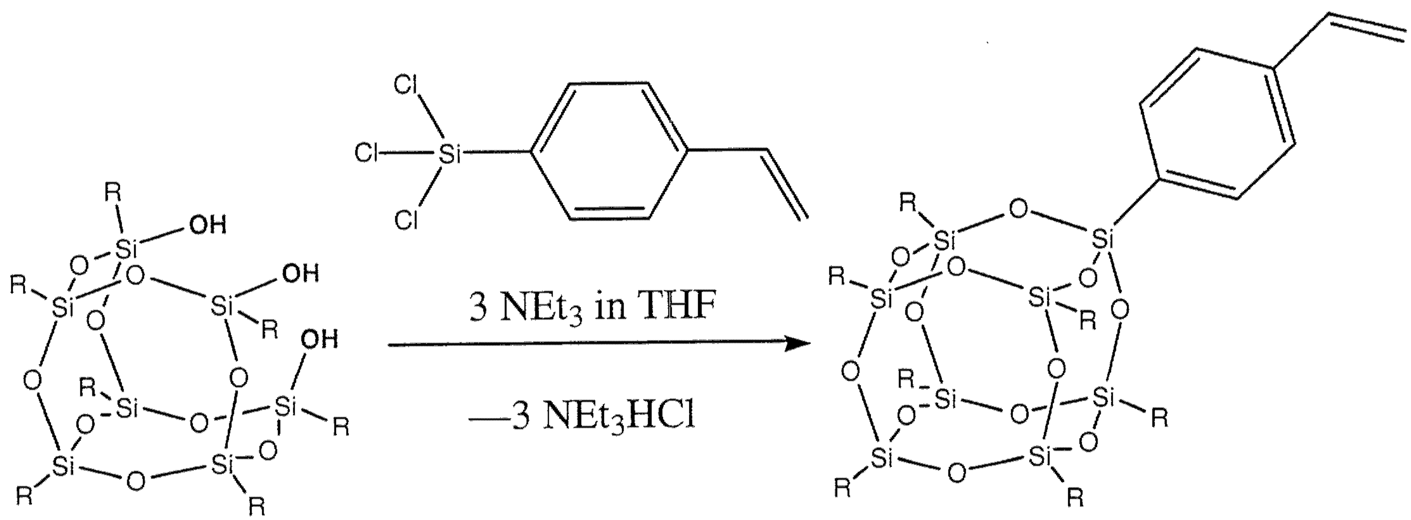
Hsiao, AFRL

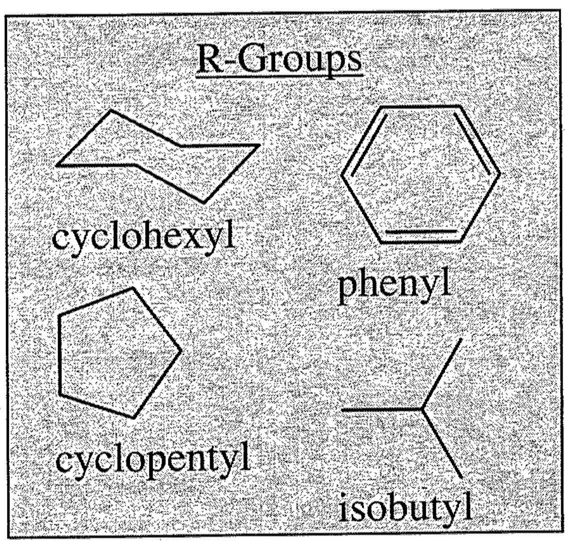
POSS Rubbery Copolymers

- POSS significantly enhances thermal mechanical properties of rubbers
  - 50 wt% POSS leads to a 25˚C increase in T_g and retains structural integrity at elevated temperatures.
  - 30 wt % cyclohexyl POSS doubles the modulus at low temperature.
  - 20 wt % cyclohexyl POSS needed to enhance the modulus of the PN relative to the POSS-free rubber.
- TEM images highlight the structure property relationship that is a function of POSS R group.
- FY03 Collaborations
  - FY03 collaboration with Pat Mather will elucidate the structure-property relationship for the full suite of POSS R groups.
  - FY03 collaboration with Andre Lee to compare blending Vs. grafting in POSS-Kraton TPE's.
  - FY03 collaboration with Brian Coughlin to begin investigating POSS EPDM copolymers as compatibilizers between POSS blendables and EPDM

POSS Pendent
Glassy Polymers

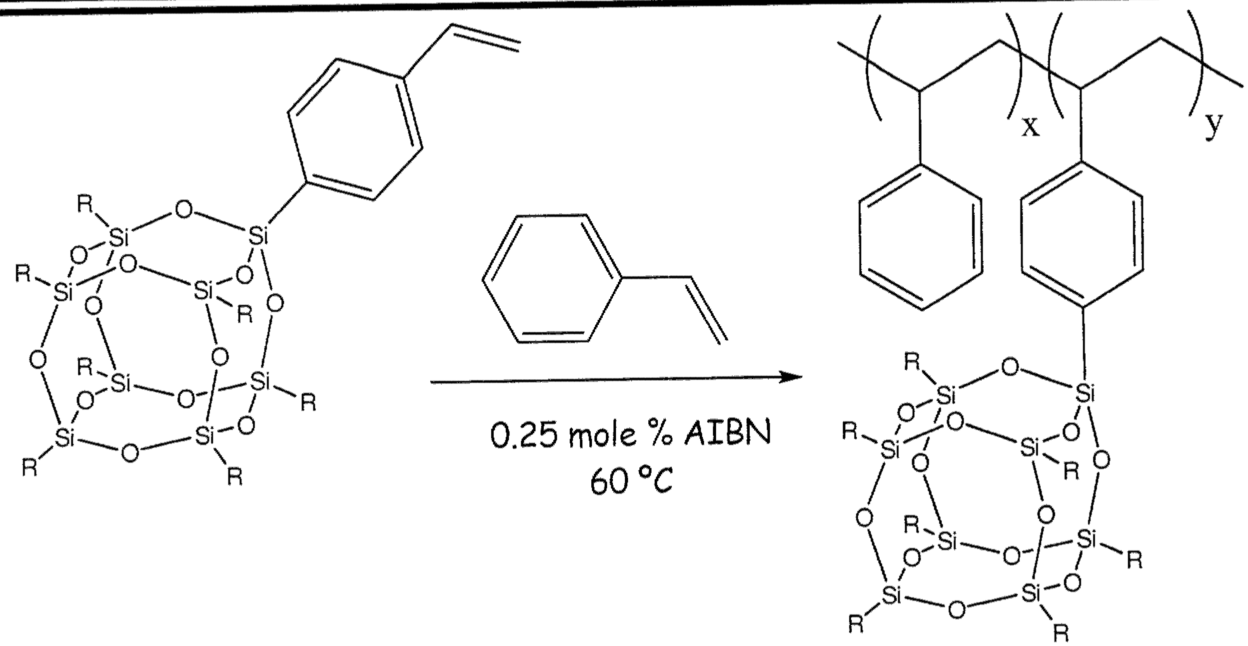
POSS Styrene Monomer Synthesis





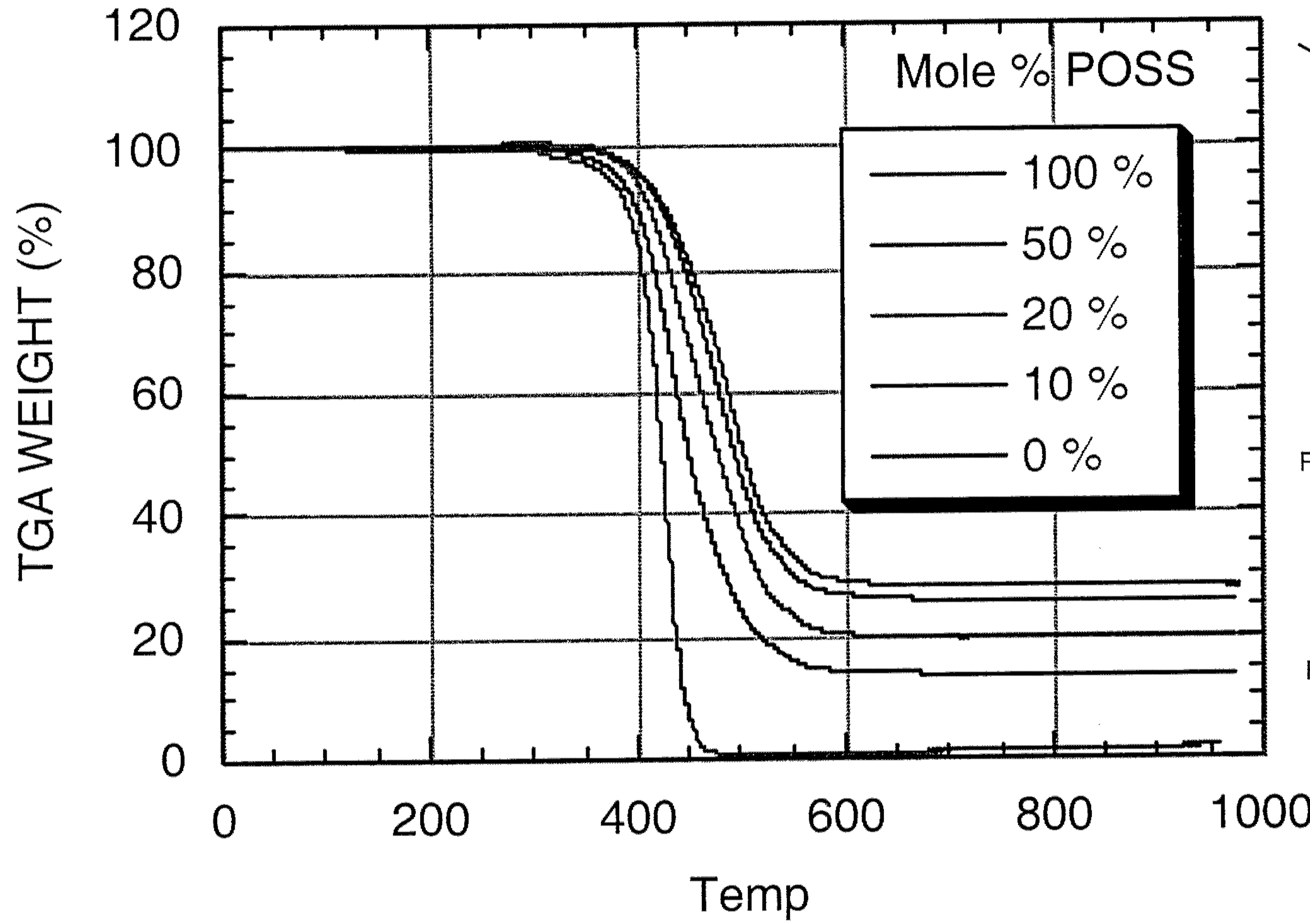
- High-yield syntheses
- Phenyl derivative requires inverse addition
- J. Inorg. Organomet. Polym., Vol 11, 2002, p. 155

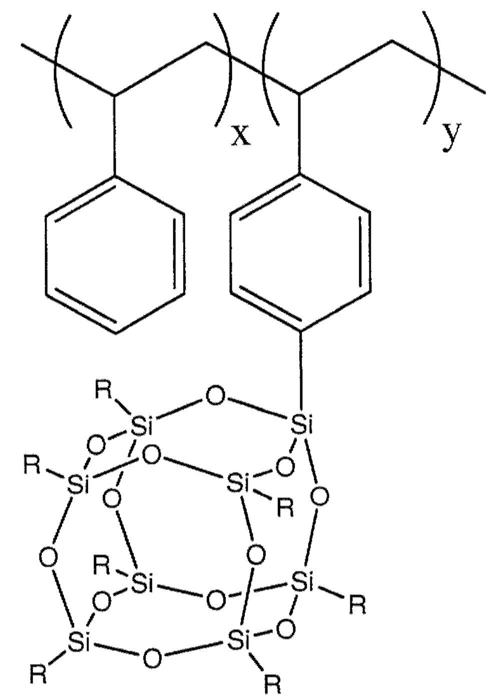
POSS Styrene Copolymer Synthesis



- Solution polymerization in toluene or bulk polymerization possible
- Polymerization is limited by solubility of the POSS-macromer
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble
- Macromolecules Vol. 29, 1996 p. 7302

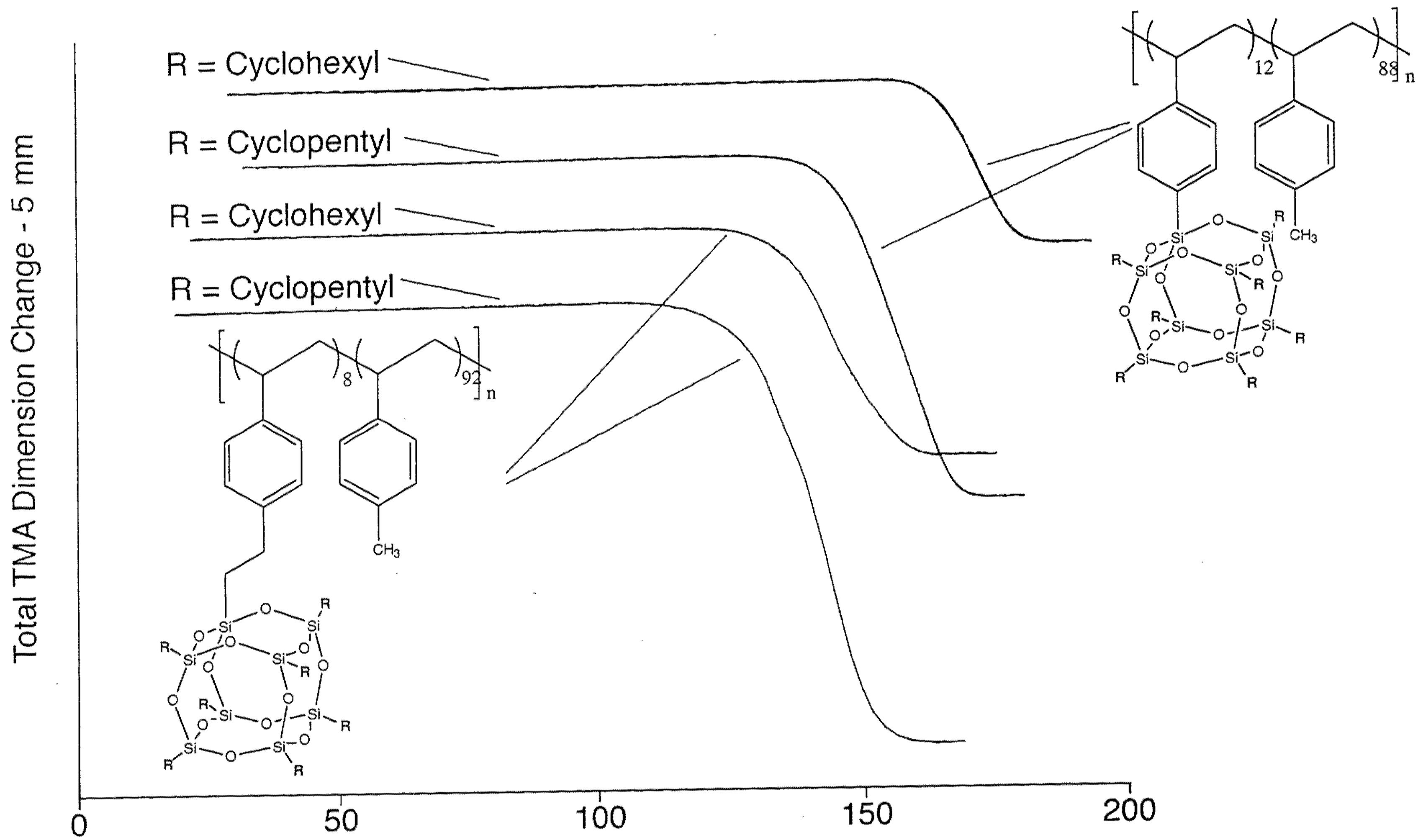
TGA Data for POSS Styryl Polymers





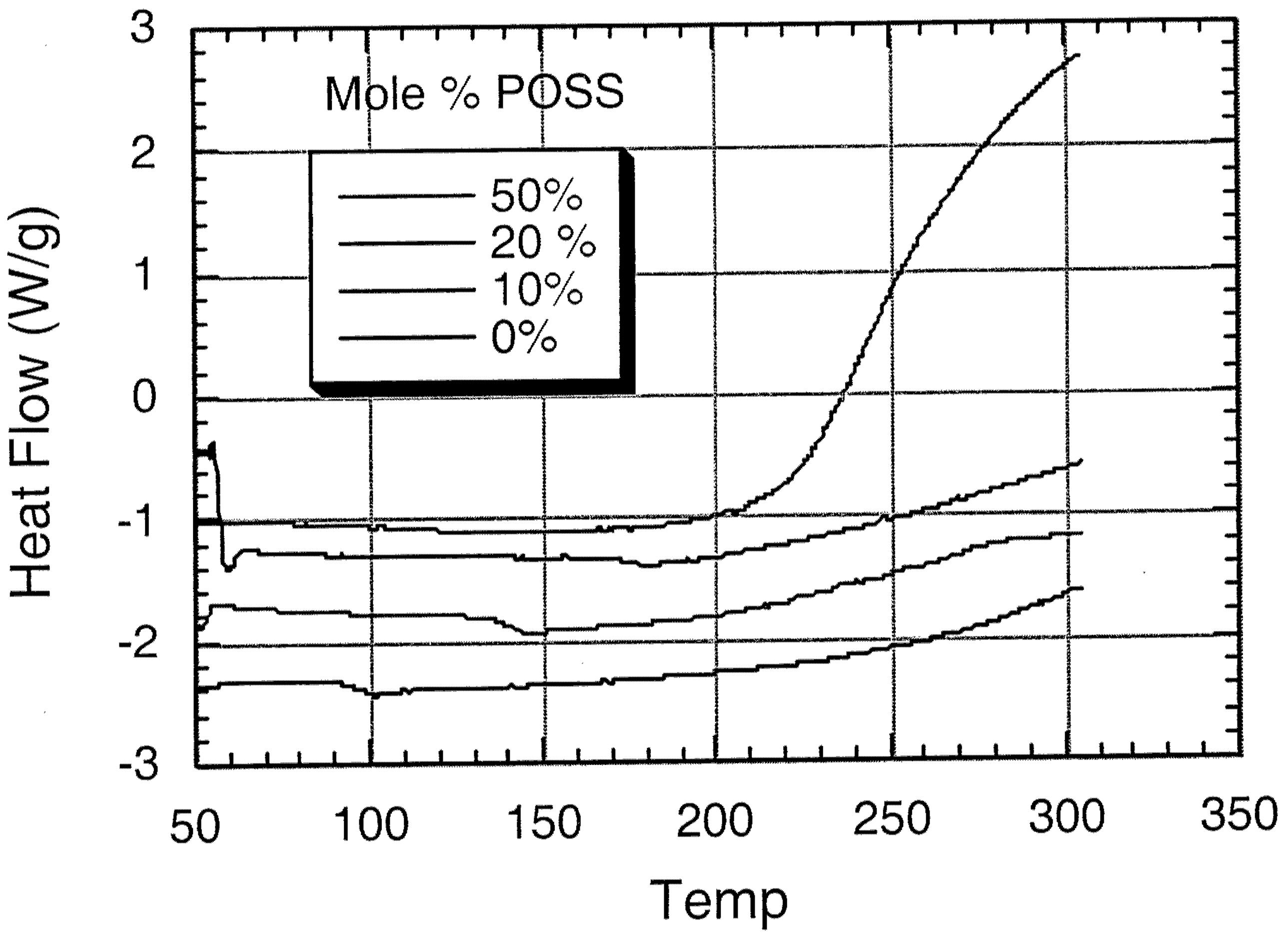
$R = C_6H_{11}$

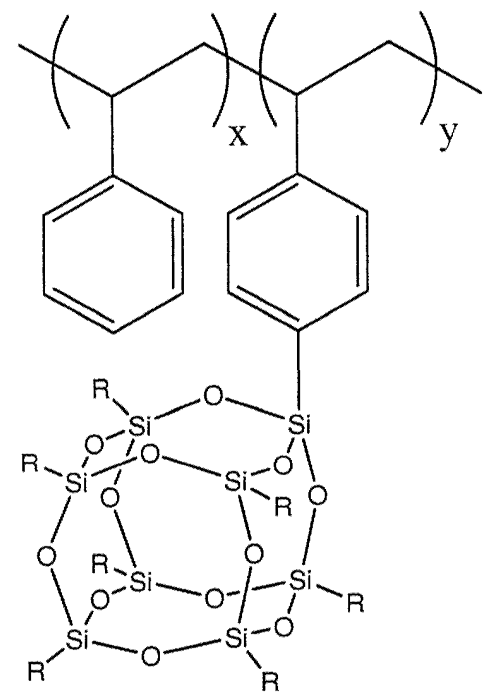
TMA Comparison: POSS Group Effect



Low DP Solution Polymerized Materials

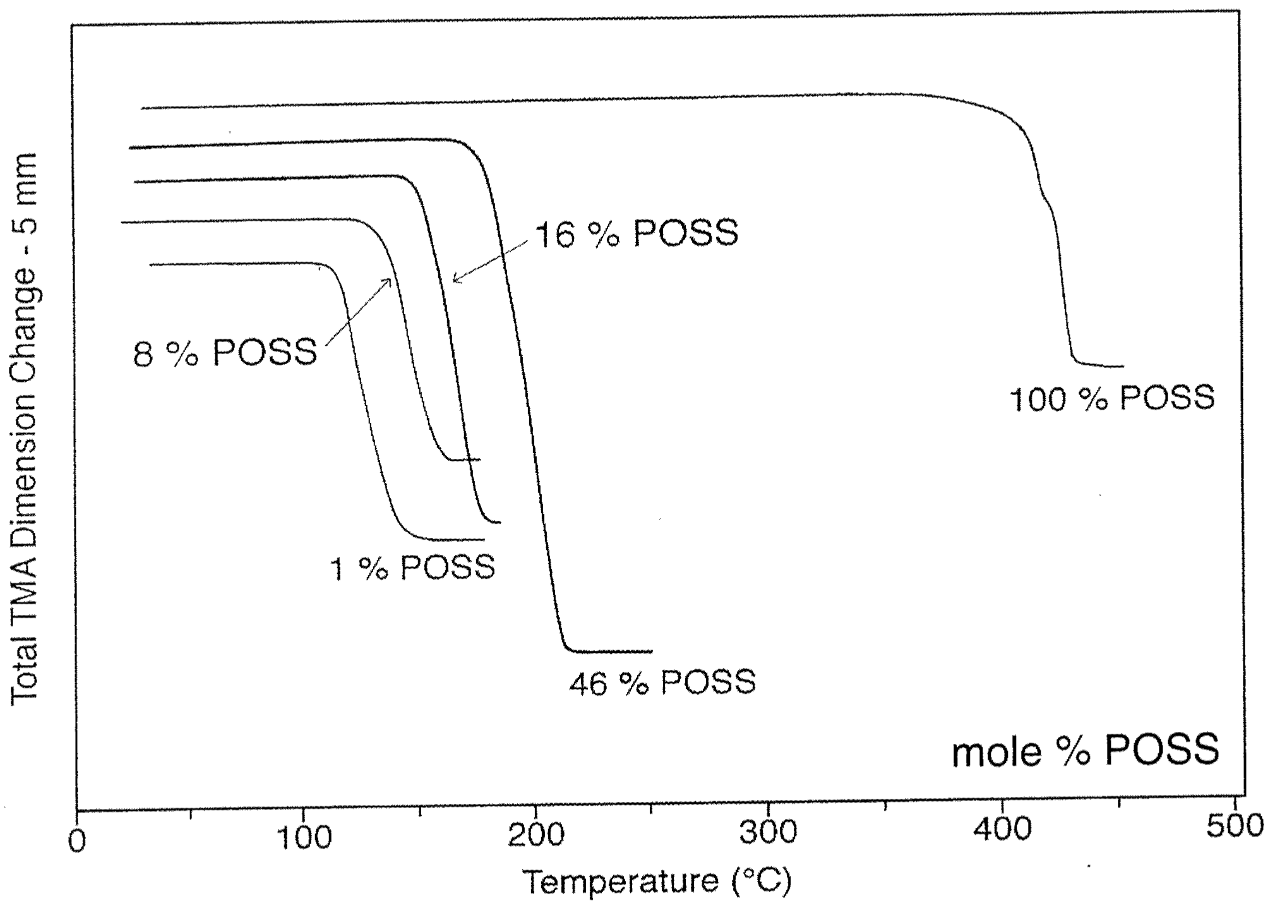
DSC Data for POSS Styryl Polymers

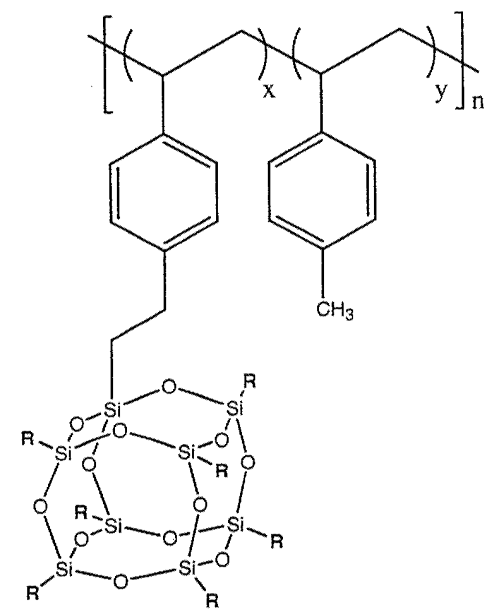




$R = C_6H_{11}$

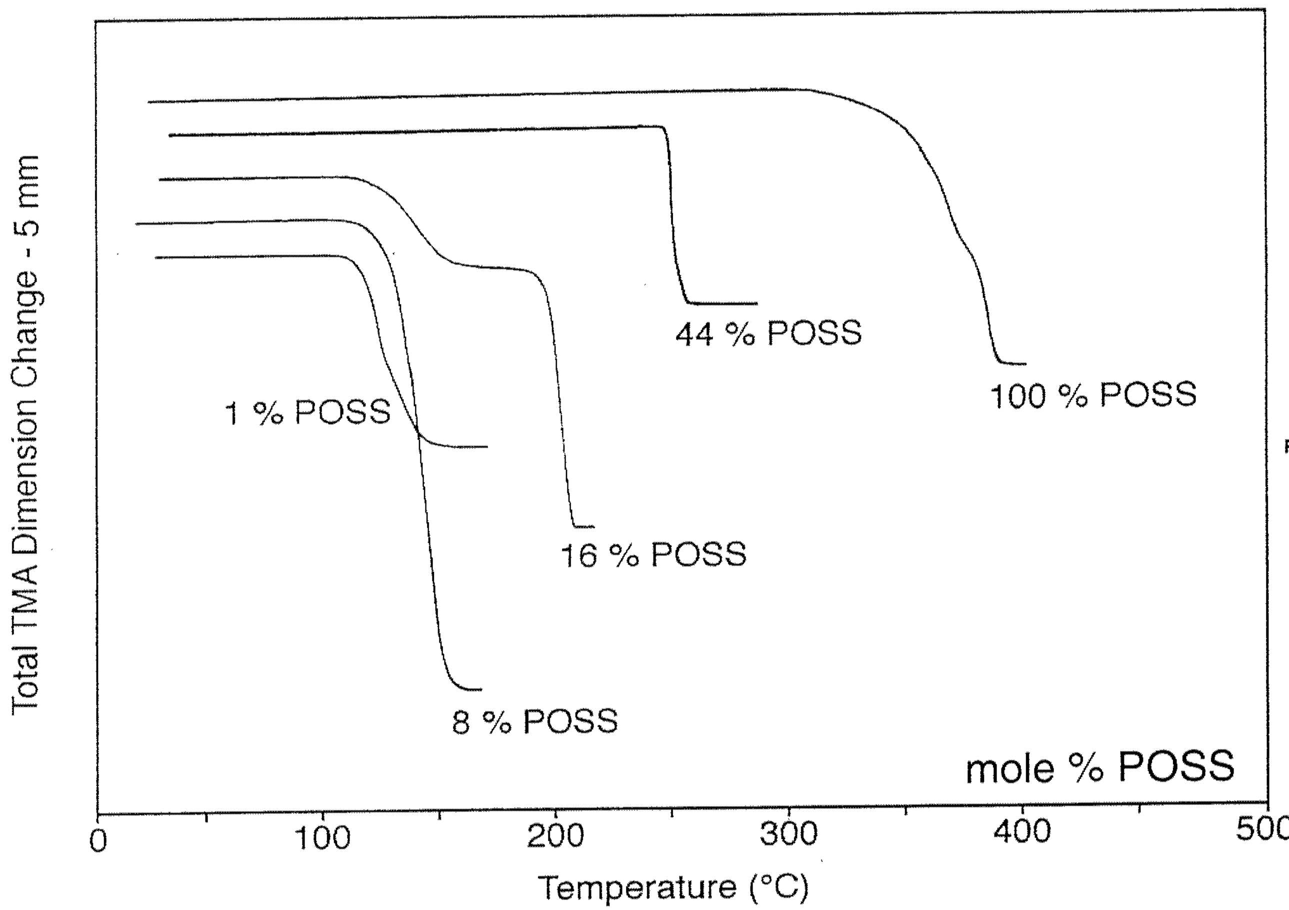
TMA Plot For POSS Styrenes (R = Cyclohexyl)

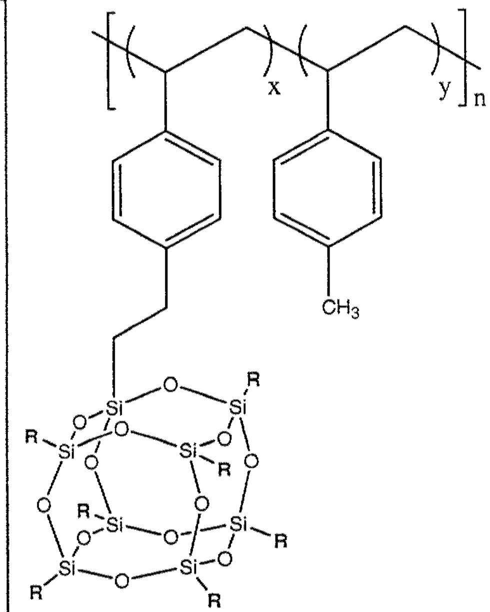




$R = C_6H_{11}$

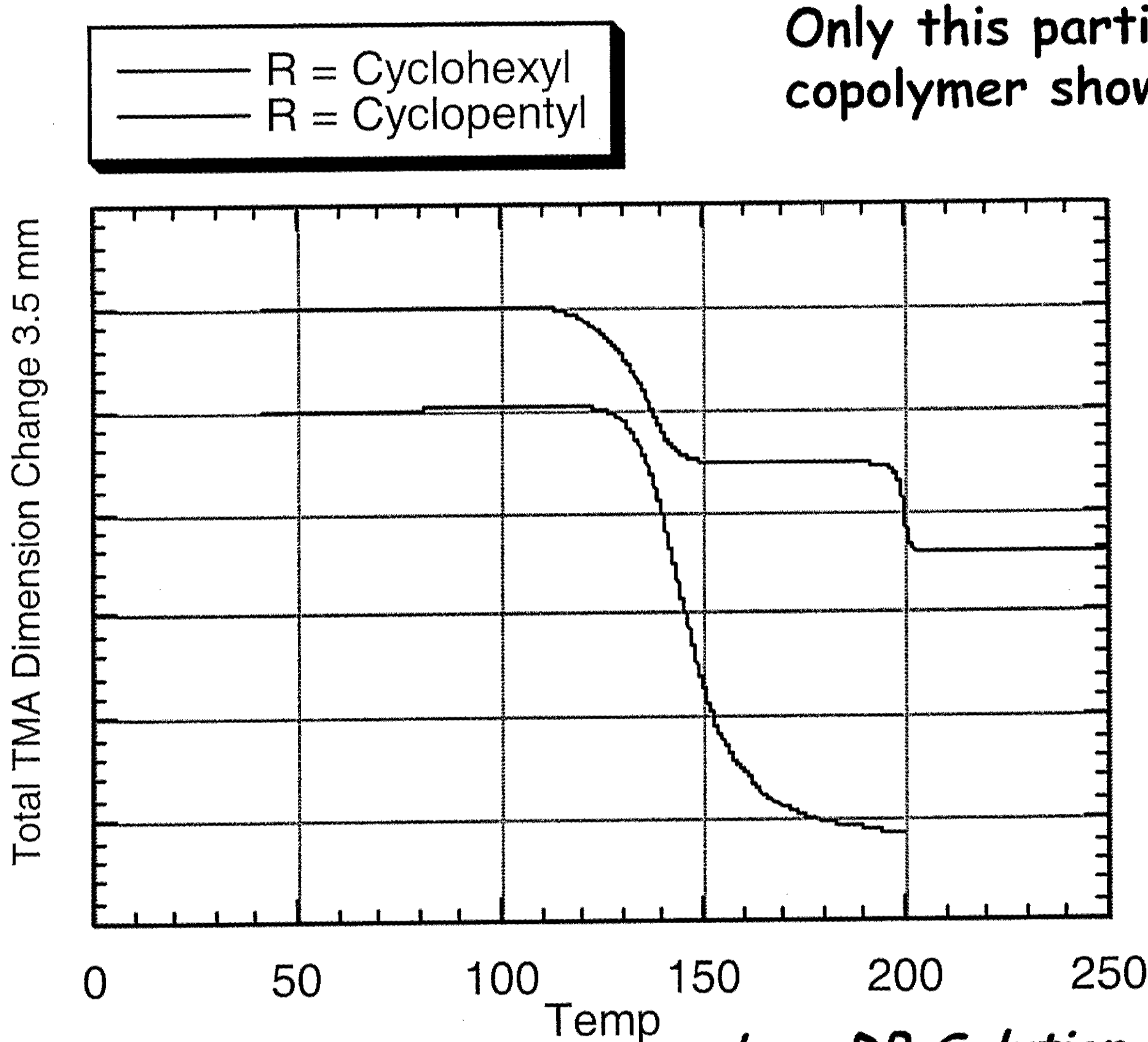
TMA Plot For POSS Styrenes (R = Cyclopentyl)



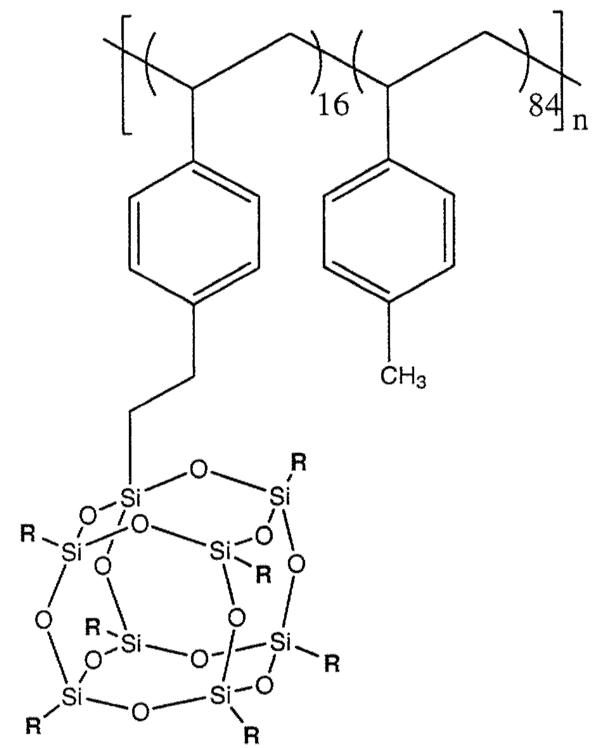


$R = C_5H_9$

TMA Evidence for a Blocky Copolymer

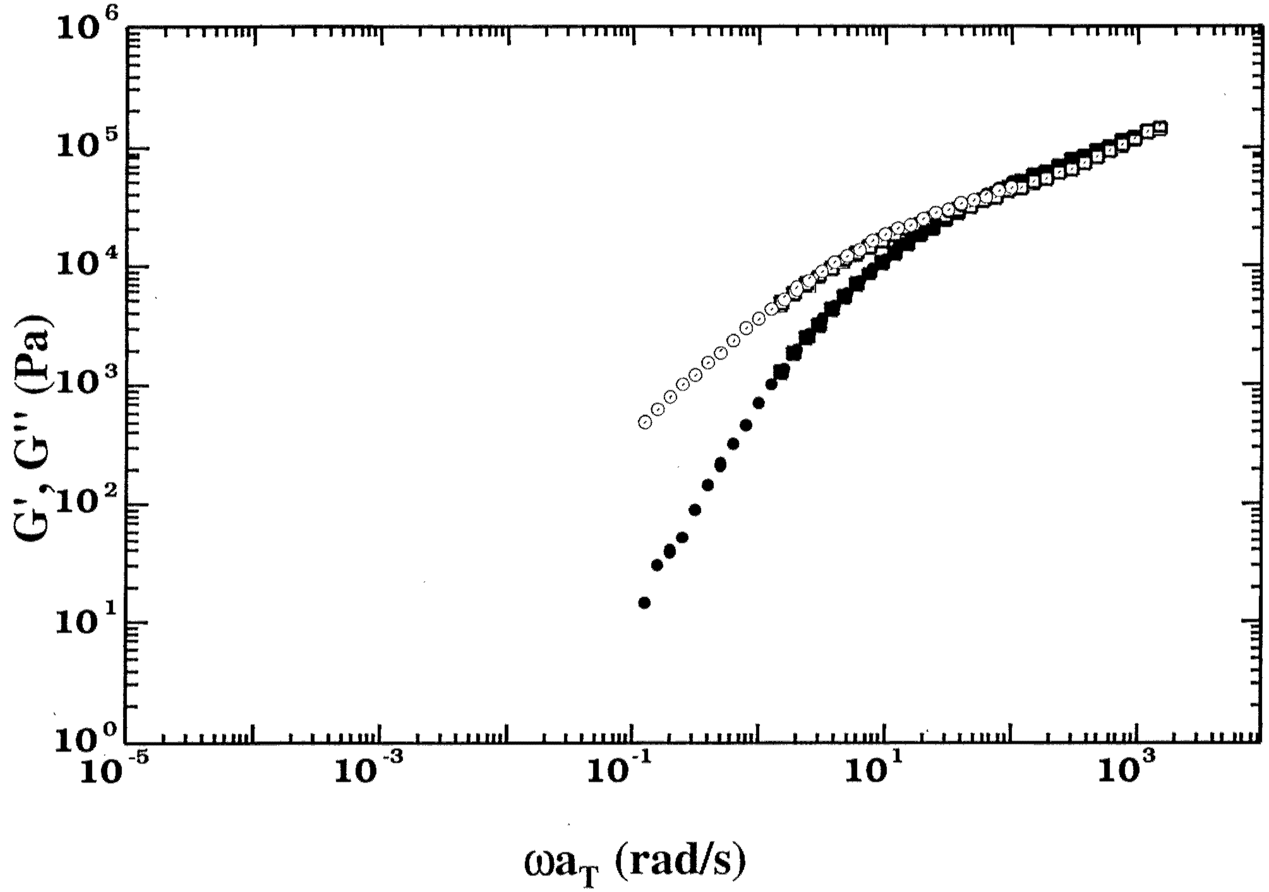


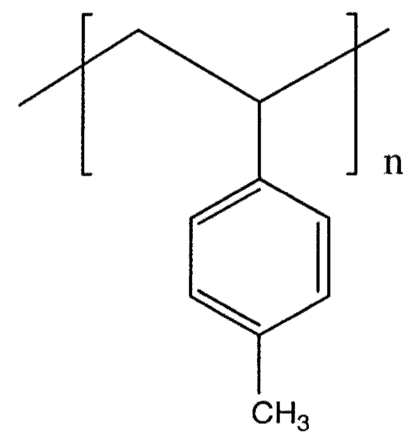
Only this particular cyclopentylPOSS copolymer shows two transitions.



Low DP Solution Polymerized Materials 56

Rheology of Unentangled PolyStyrene



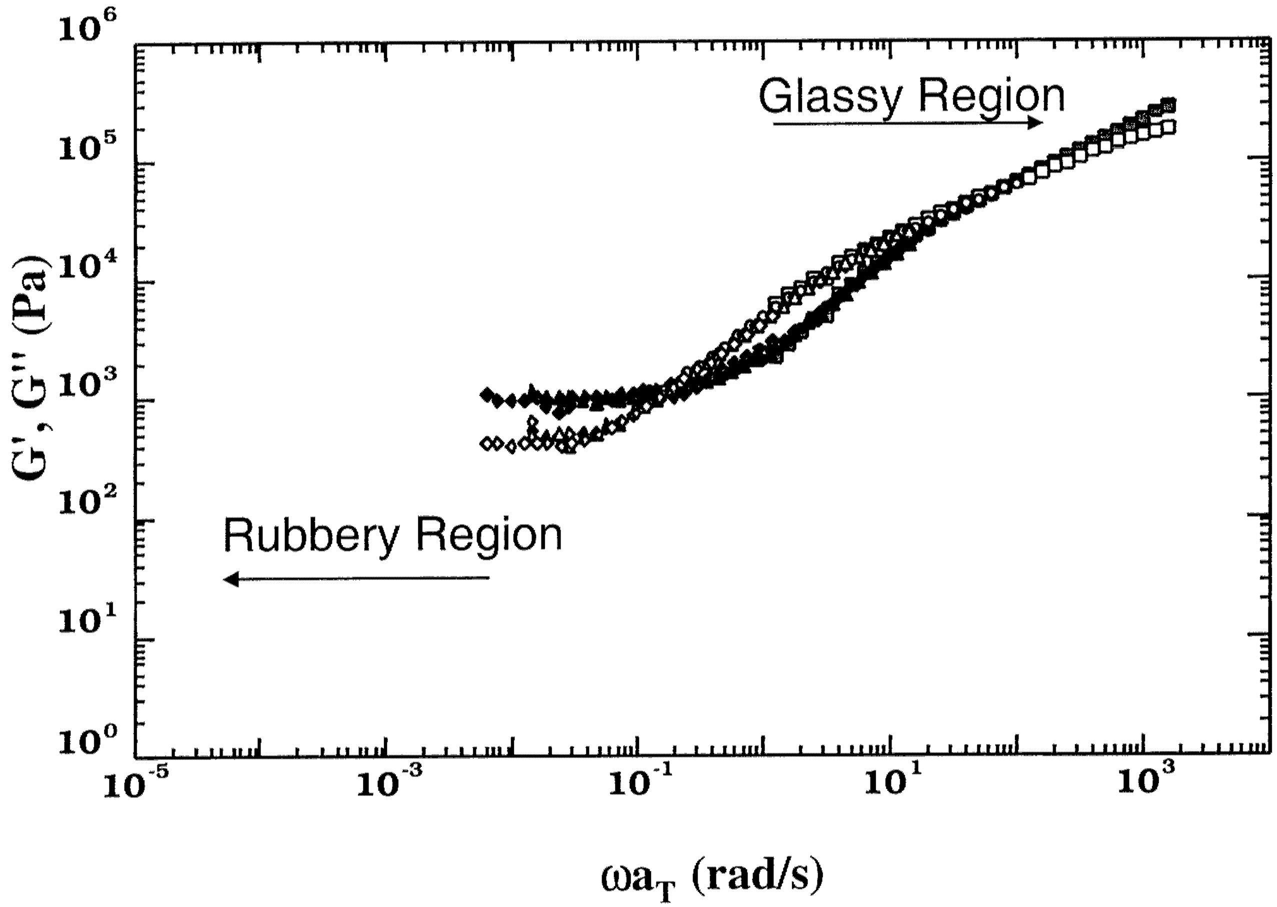


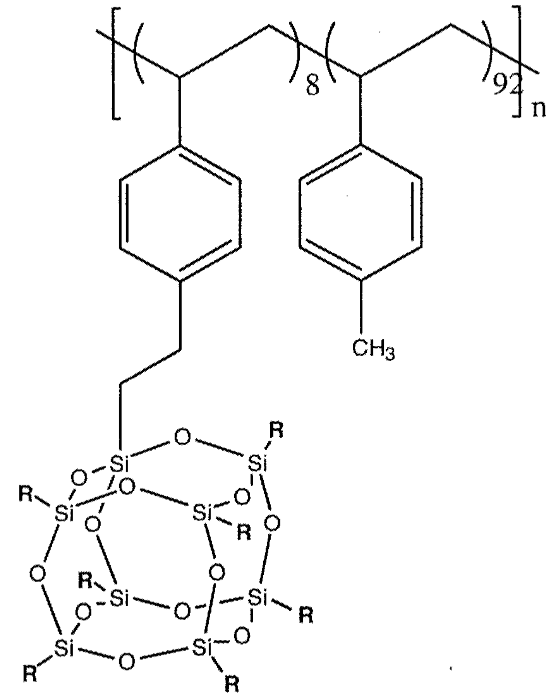
Tg = 119 C
Mn = 21 K
Dp = 178

Low DP Solution Polymerized Materials

Pat Mather, AFRL

Rheology of a 8 Mole % POSS Polymer

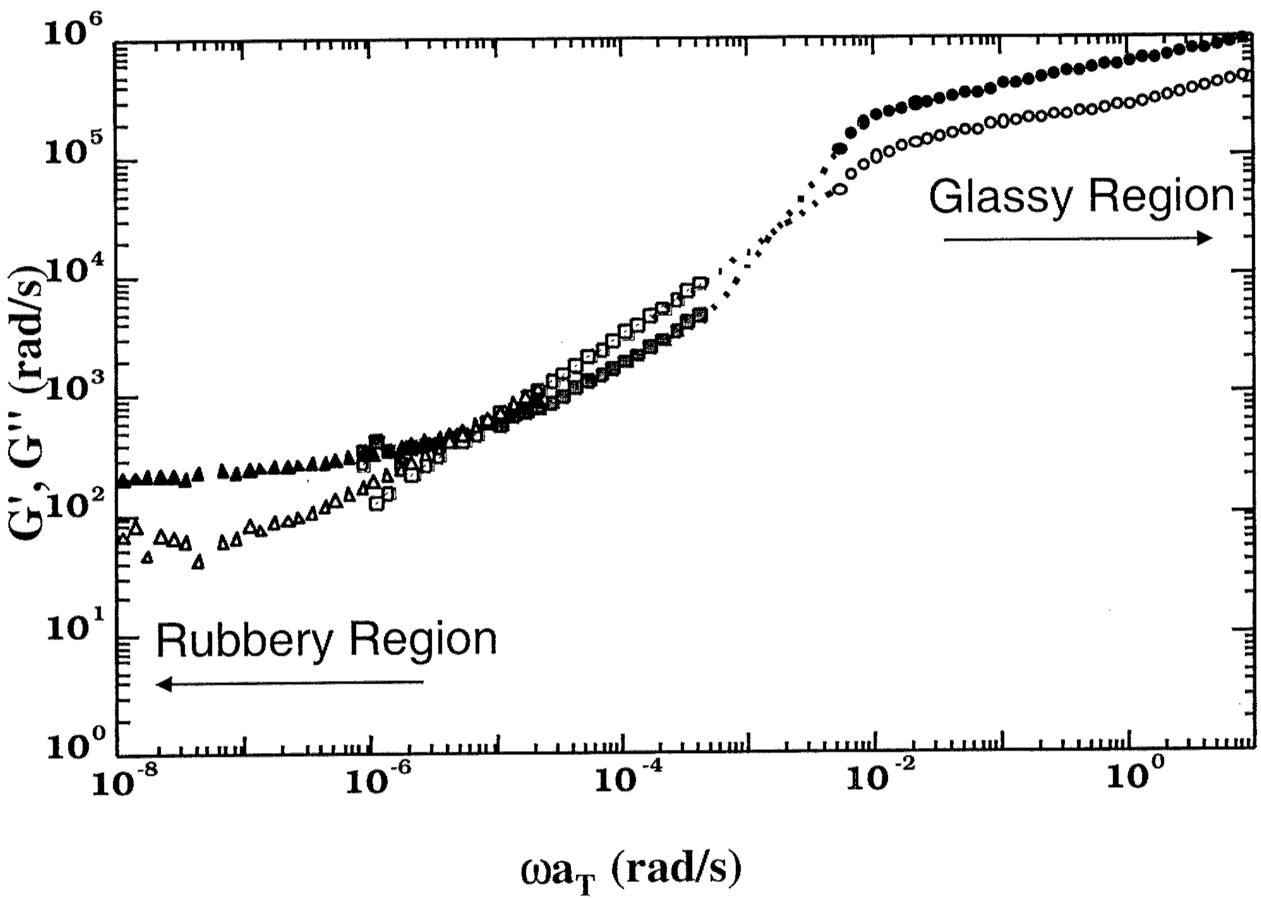


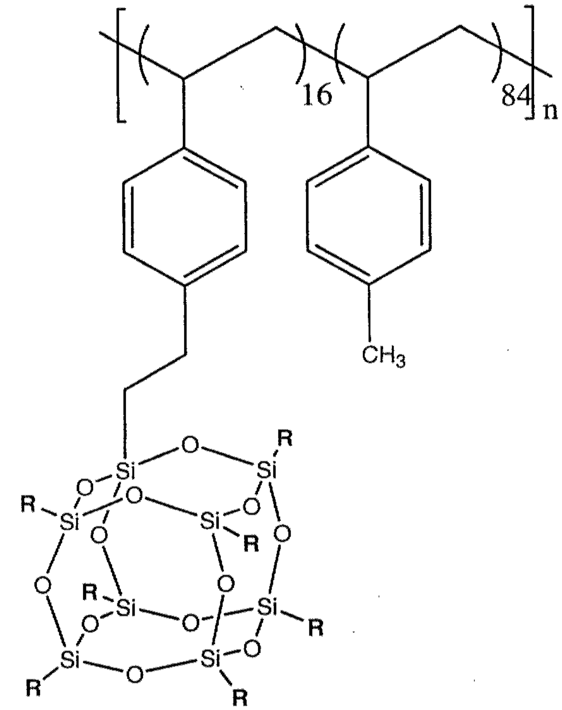


$R = C_6H_{11}$
Tg = 136 C
Mn = 72 K
Dp = 360

Low DP Solution Polymerized Materials **Pat Mather, AFRL**

Rheology of a 16 Mole % POSS Polymer





R = C_5H_9
Tg = 126 C
Tg = 199 C
Mn = 42 K
Dp = 160

Low DP Solution Polymerized Materials

Pat Mather, AFRL

Reactivity Ratio For POSS Styrene

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$
$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$
$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$
$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

These reactivity ratios were determined by analysis of seven polymerizations, which yielded 21 pairs of equations and the two variables (r_1 and r_2)

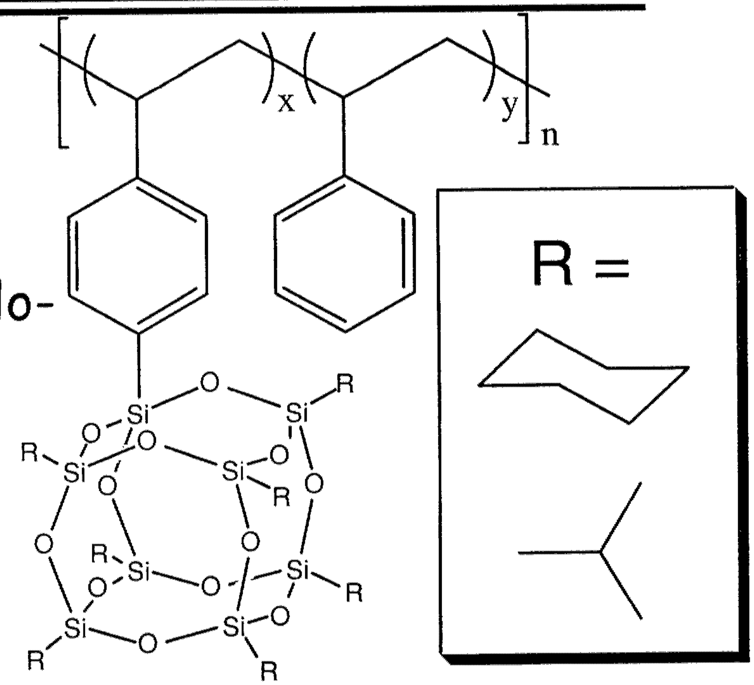
Data by ^1H NMR
r_1 Styrene = 1.09
r_2 POSS-Styrene = 0.34

Data by FTIR
r_1 Styrene = 1.19
r_2 POSS-Styrene = 0.17

Reactivity ratios show that random copolymers are to be expected

Solubility of High Molecular Weight Copolymers

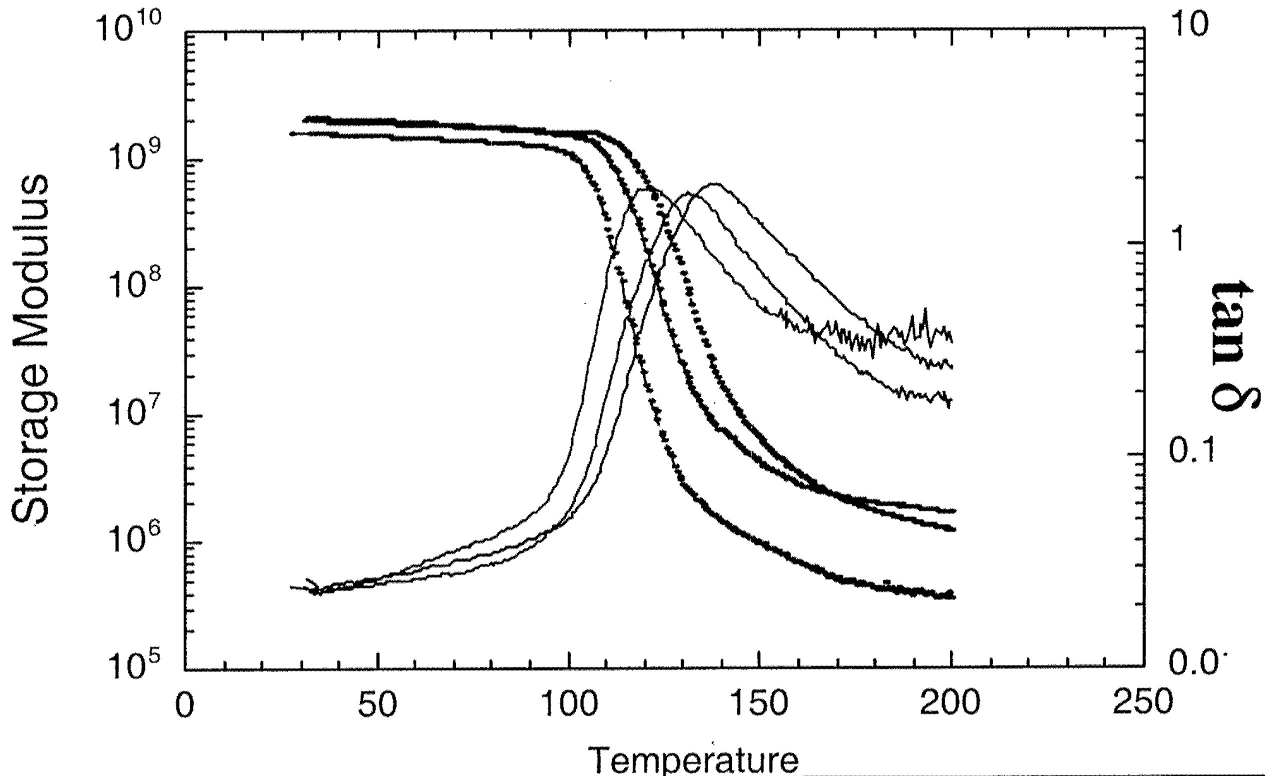
Both bulk and solution polymerization methods were used to find that highly entangled POSS-polystyrene can form an insoluble gel. If the R-group is cyclohexyl, then this gel effect occurs at very low POSS content. Much higher loadings of isoButylPOSS are required to obtain similar insoluble materials.

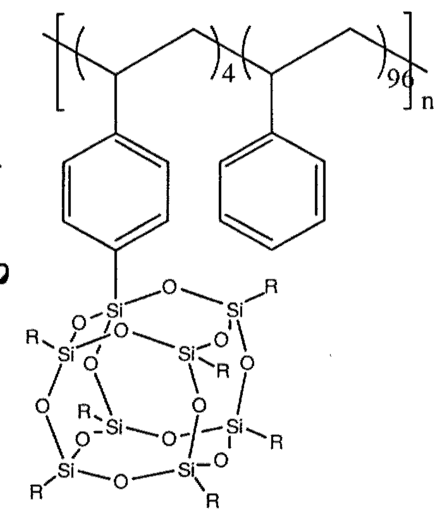


POSS-POSS Interactions can Dominate to form insoluble *"Gels"*

POSS type	Degree of polymerization	Wt% POSS	Styrene/POSS
Cyclohexyl	> 3000	5-10	~150:1
isoButyl	~4000	35-40	~17:1

DMA of 30 Wt. % POSS Polystyrenes





- Comparison of isobutyl, cyclopentyl & cyclohexyl
- High Molecular Weight Bulk polymerized samples

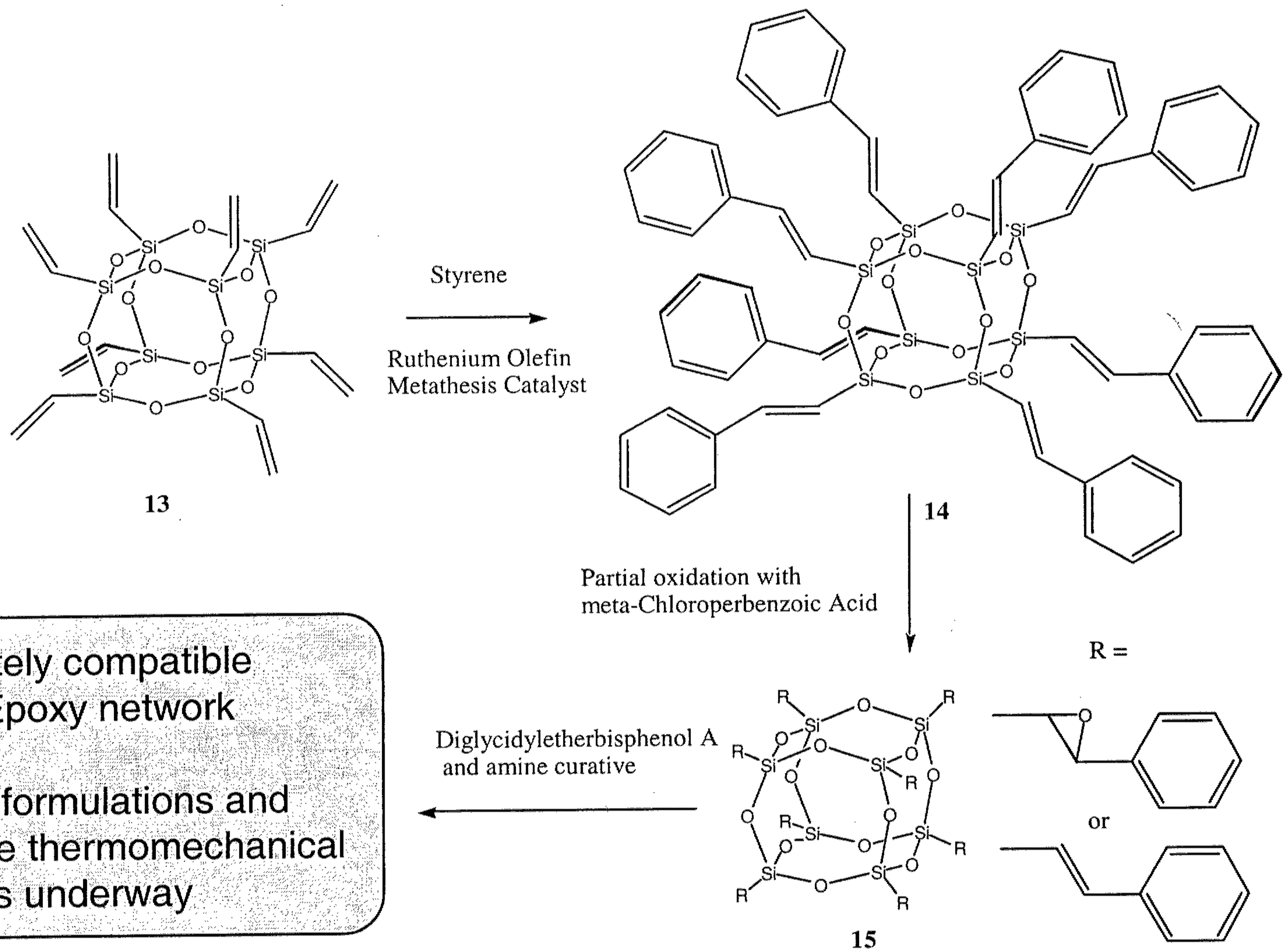
Continue this collaboration with Pat Mather

POSS Glassy Copolymers Summary

- The aforementioned results for POSS-polystyrenes are mirrored by POSS-acrylics
- Thermal properties of PS are greatly enhanced by POSS incorporation
  - Softening temperature can be raised to 325 °C!
- POSS enhancements are R-group dependant
  - Below 50 wt % cyclohexyl has a stronger effect than cyclopentyl
- Rheology revealed a rubbery plateau modulus caused by POSS-POSS physical crosslinks
- Future Work: FY03 Mechanical Properties of High MW polymers will be obtained

POSS Thermosets

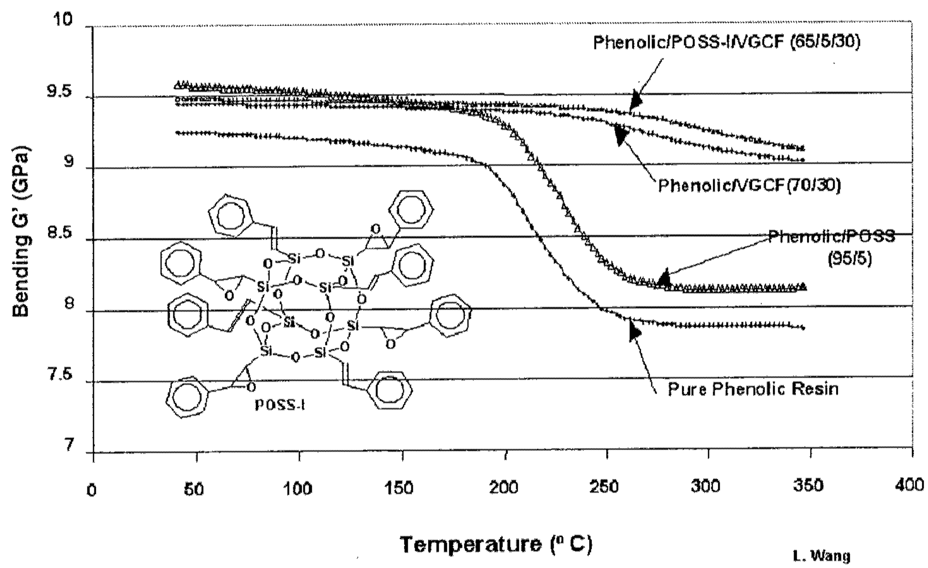
Synthesis of Polyfunctional POSS Epoxys

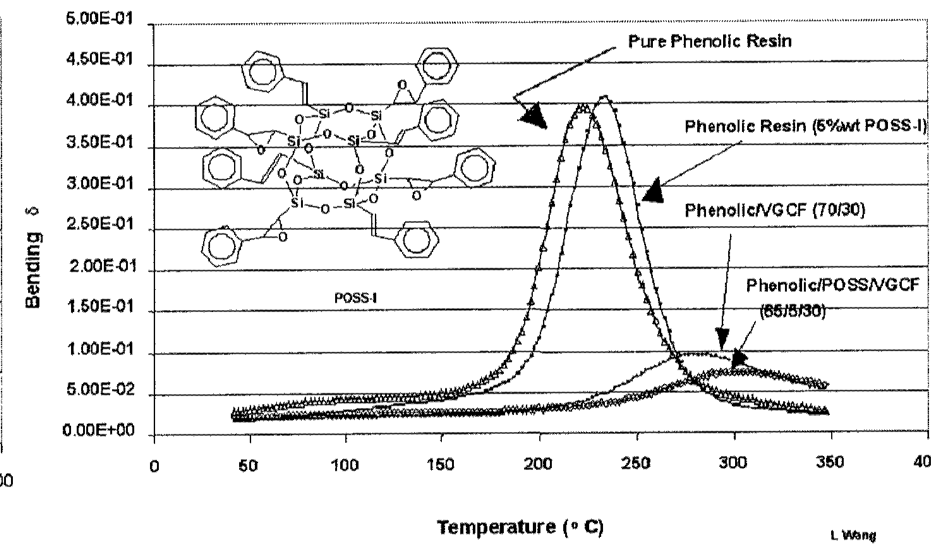


Completely compatible POSS-Epoxy network

Several formulations and complete thermomechanical testing is underway

Charles Pittman POSS Phenolics

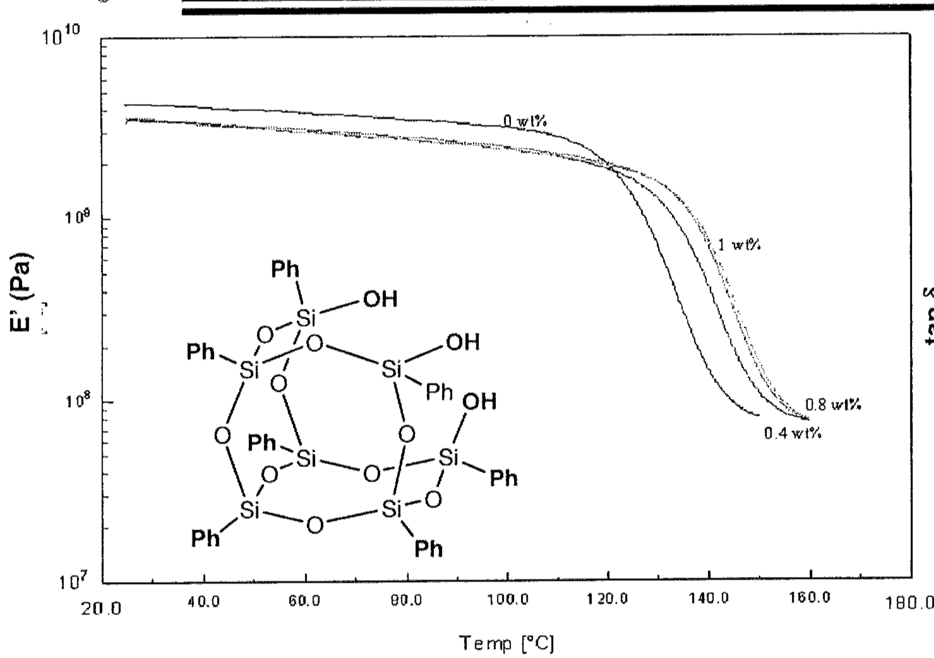


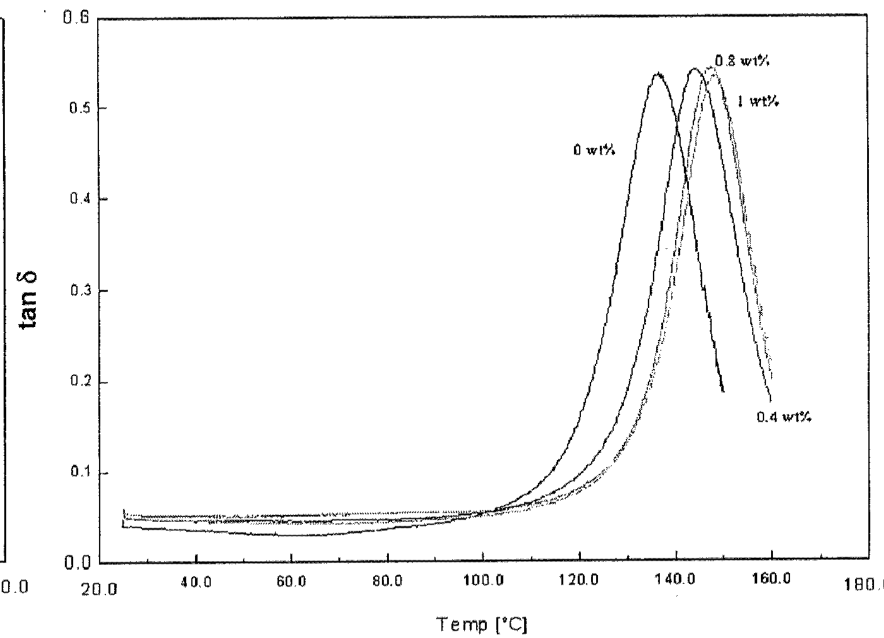


POSS-phenolic thermosets- with and w/o VGCF

5 wt% POSS raises T_g 10˚C
30% VGCF raises T_g 55˚C
30% VGCF and 3.5% POSS raises T_g 80˚C !!!

Andre Lee DER 332 Aircraft structure Epoxy

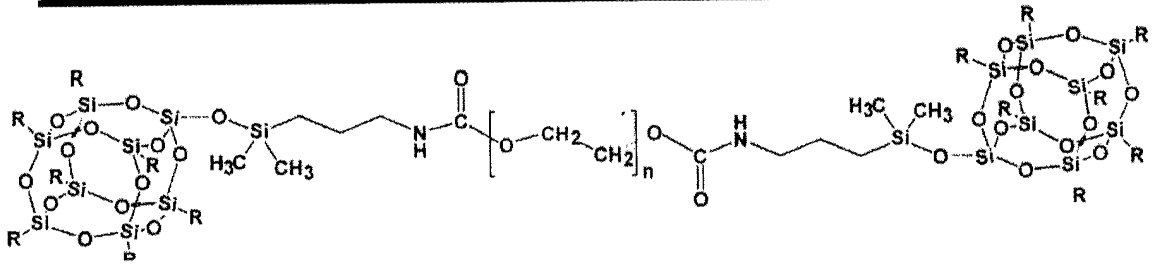




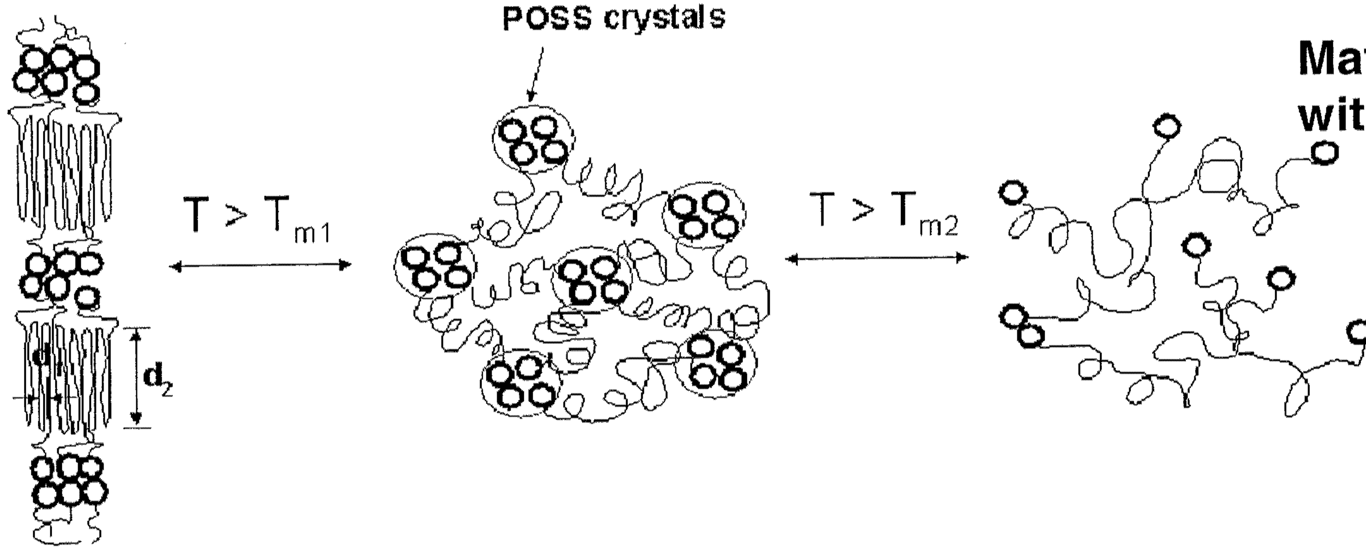
Just 1 wt% POSS causes a 5°C increase in T_g !!

POSS Semi-Crystalline Polyethylene Oxides

Pat Mather: Semi-Crystalline POSS PEO



- POSS PEOs are Amphiphilic
- Single POSS Cage acts as a block
- Mather Model agrees with Coughlin Model



Two crystalline domains:
1) PEG10K crystals (T_{m1})
2) POSS crystals (T_{m2})

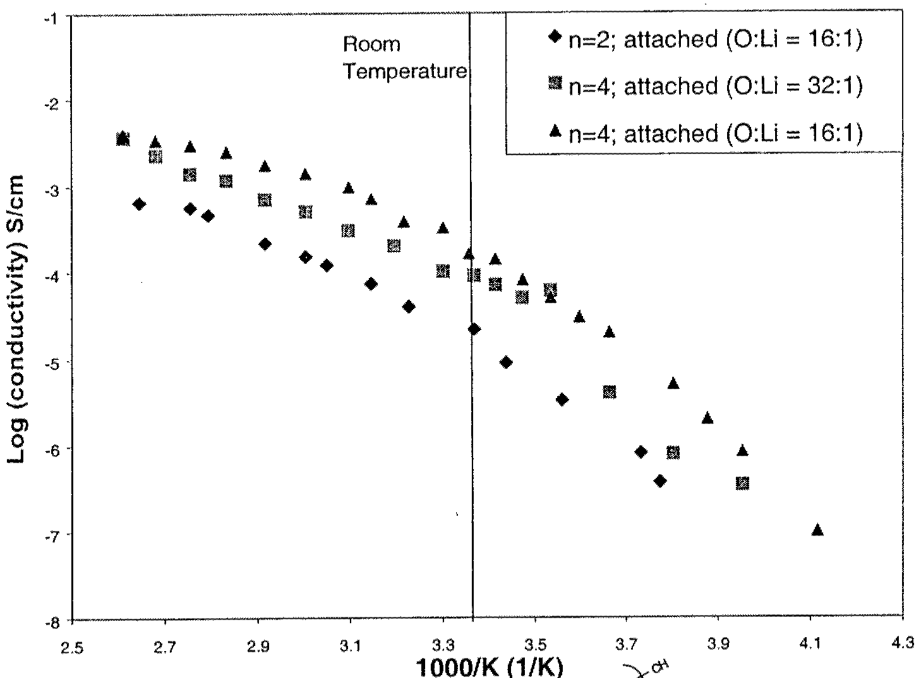
Rubber-like behaviors
(A physical network
in higher temperature)

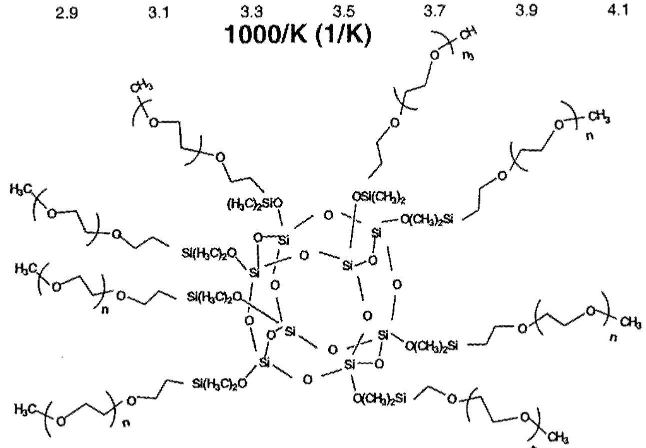
Viscous liquid-like behaviors

Mather Macromolecules 2002, 8378.

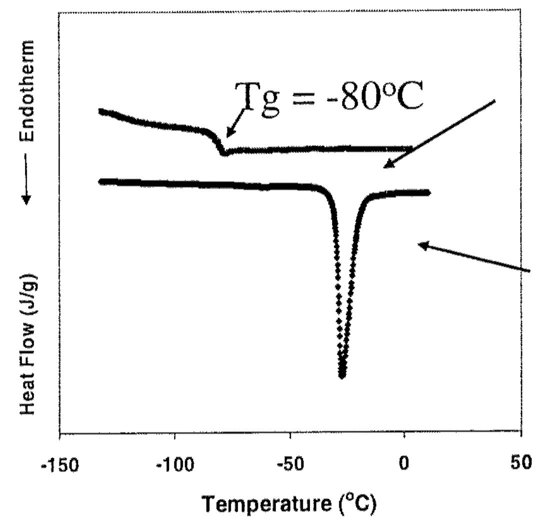
Stephanie Wunder: POSS Based PEO Electrolytes

Conductivity of $Q_8M_8^{PEO(n)}$ and $LiClO_2$





<u>DSC Data</u>: *Crystallinity completely suppressed on attachment of PEO(n=4)*



POSS PEO n=4

$H-(OCH_2-CH_2)_4-OH$

No observable Tg

Tm= -27°C

σ of PEO at RT is ~ 10^{-5}

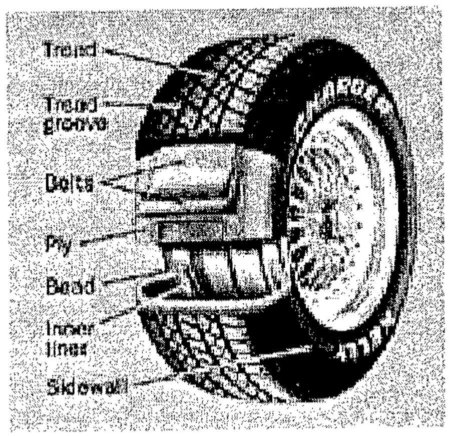
σ goal for PEO-based solid polymer electrolytes is 10^{-3}

Dave Scheraldi: POSS PET

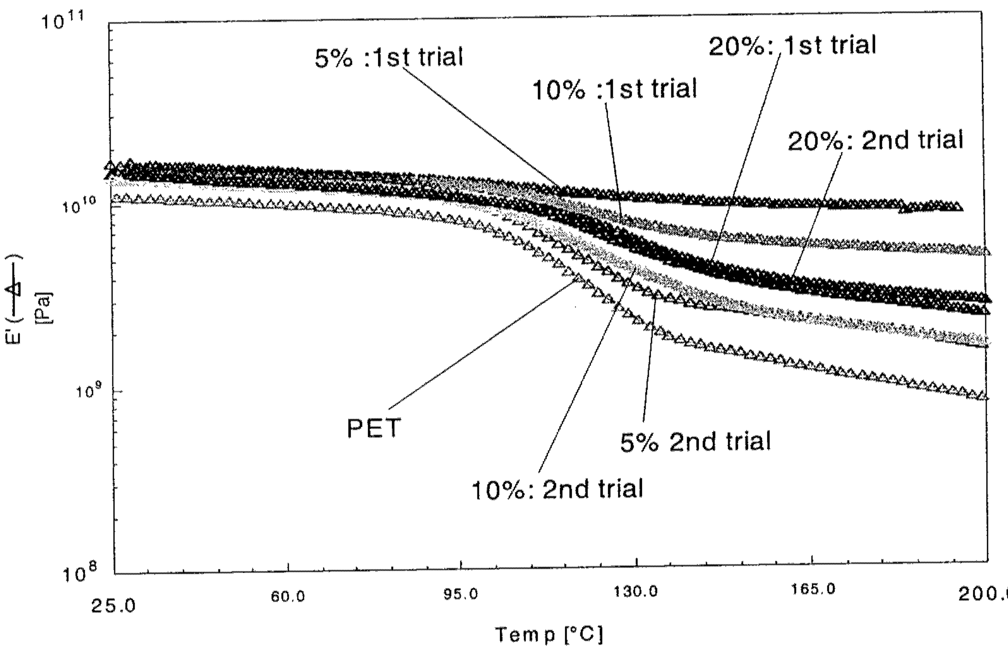
Tires are typically Reinforced with PET Fabrics

PET Tg
polymer 78° C
HMLS yarn ~ 110° C

Internal Tire Temperature
~ 120° C



TrisilanolisooctylPOSS PET Blend



Scheraldi (Case Western) and KOSA investigating processing parameters for POSS blended with PET tire cord

Masanori Ikeda: Flame resistant POSS PPE

Asahi-KASEI Corporation: Hybrid Plastics Asian Distributor

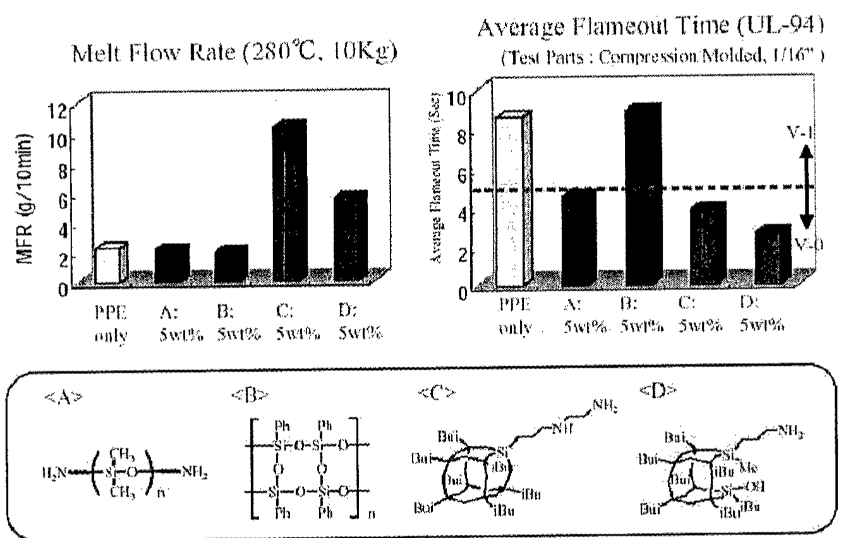


Figure 8. Effects of Additives on MFR and Anti-Flammability

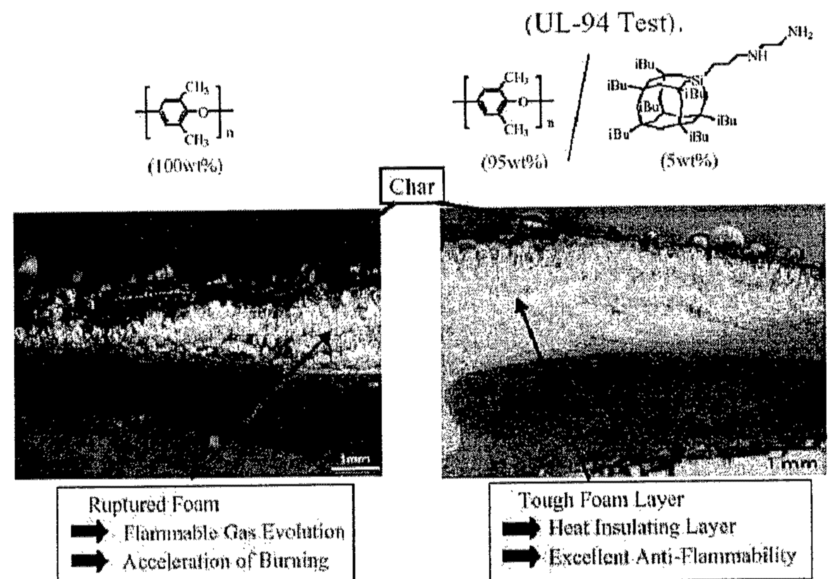


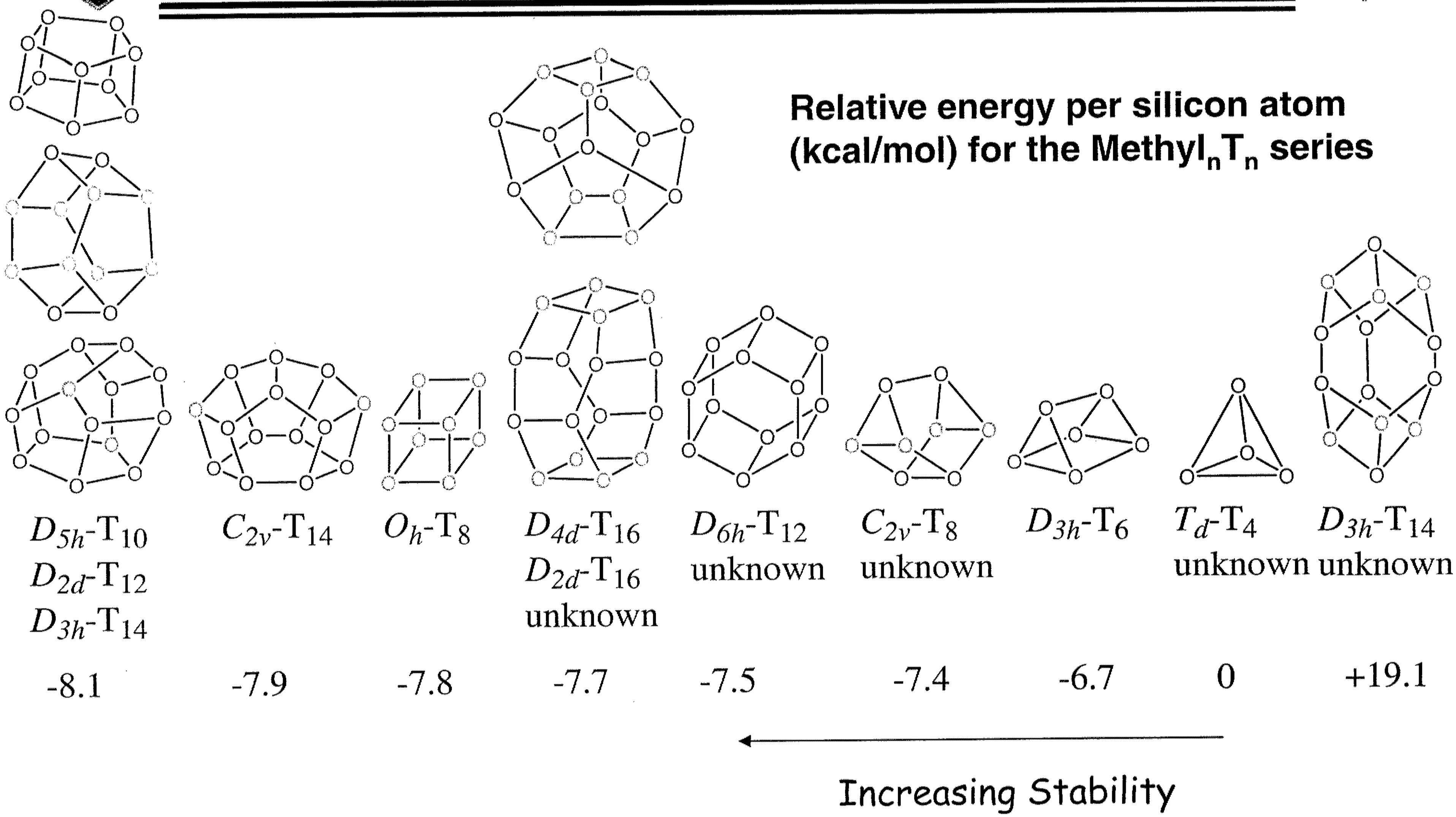
Figure 10. Cross Section Photograph of Burned Test Piece

Isobutyl POSS cage in PPE gives:
superior flame retardance
imparts superb processability
excellent HDT is maintained

POSS Modeling and Simulation

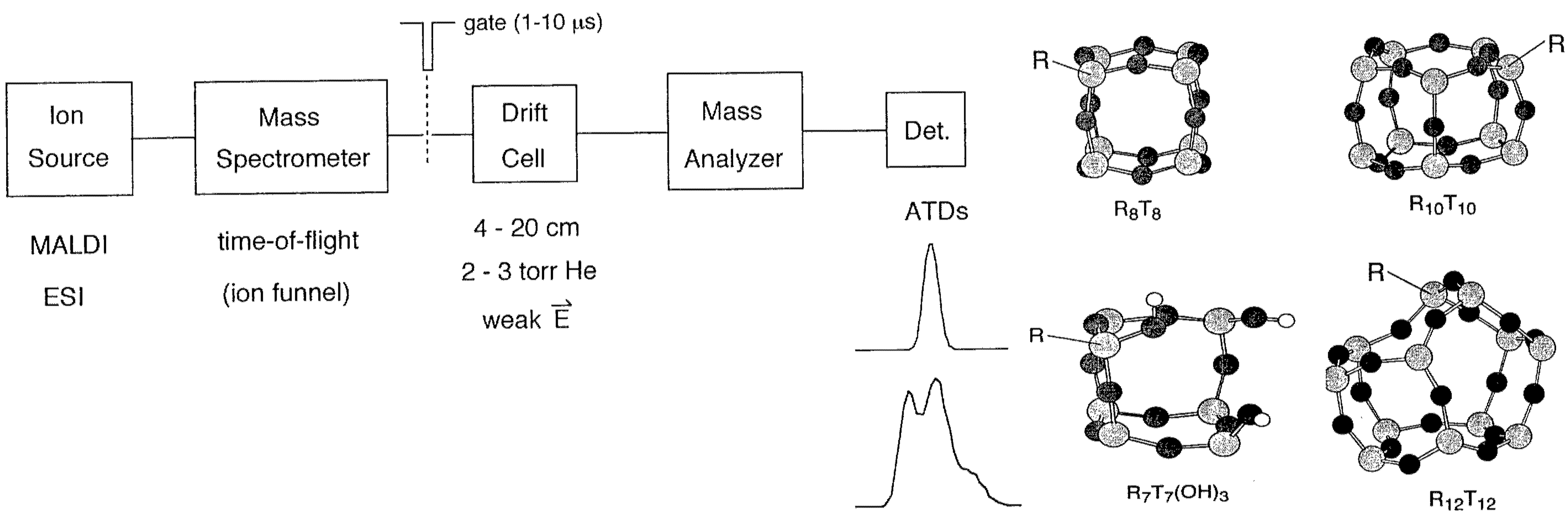
Ravindra Pandey: Ab Initio POSS Calculations

Relative energy per silicon atom (kcal/mol) for the Methyl$_n$T$_n$ series



Pandey J. Phys. Chem., 2002, 1709.

Mike Bowers: POSS MALDI-TOF



EXPT: ATDs ⟶ mobilities (K) ⟶ collision cross-sections (Ω)

$$v_d = \frac{l}{t_d} = \mathbf{K \cdot E} = \frac{\mathbf{C}}{\Omega}$$

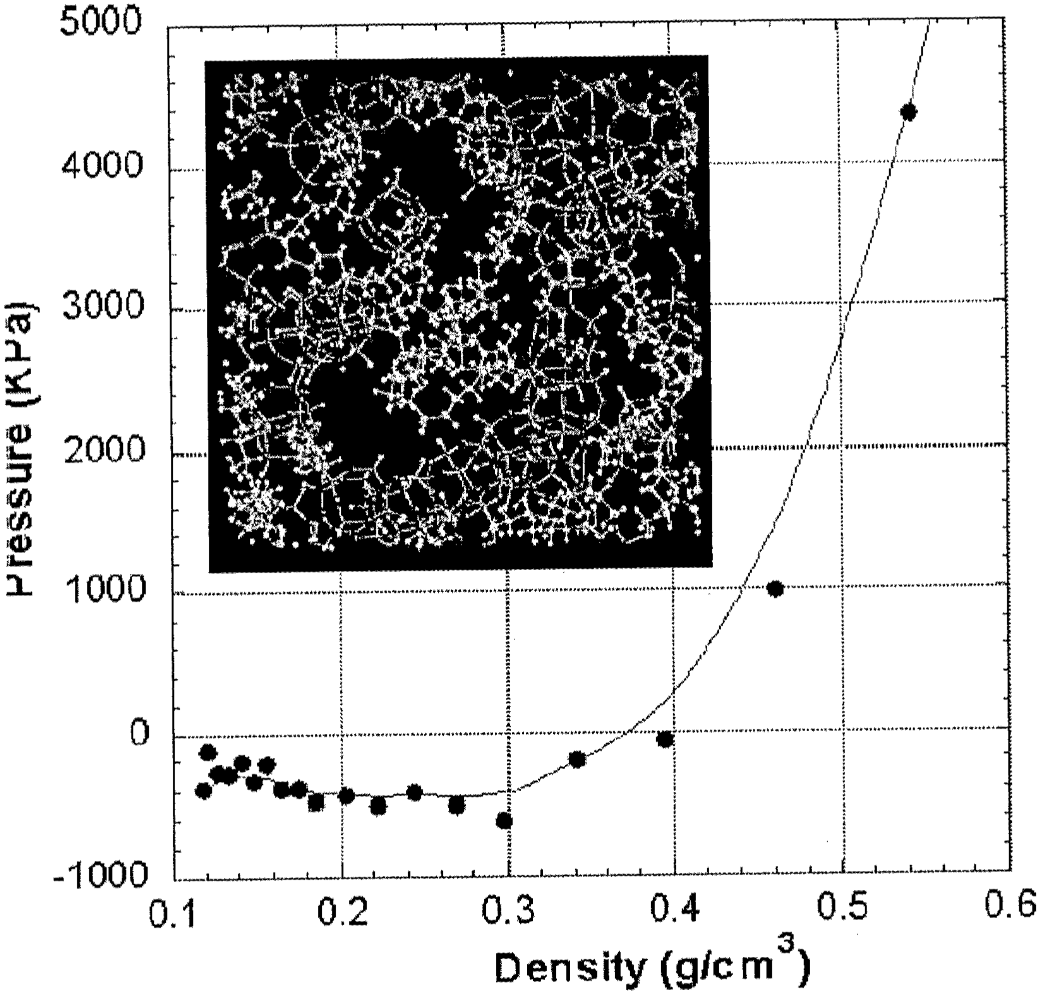
THEORY: molecular mechanics (AMBER) ⟶ structures ⟶ collision cross-sections (Ω)

Mark Gordon: Ab Initio POSS Calculations

- Calculations on POSS synthesis
- Calculations on POMS synthesis
- Calculations on POSS cages and permeability to N_2 and O_2

Gordon: J. Phys. Chem. A, 2002, 11276; J. Phys. Chem. B, 2002, 11764.

John Kieffer: POSS Simulations



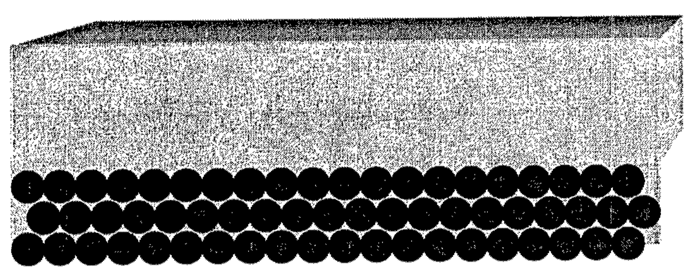
POSS tethered with decane chains agglomerate based on cage-cage and chain-chain attractions. There is an apparent repulsion between cages and chains, leading to nano-segregation and a low equilibrium density.

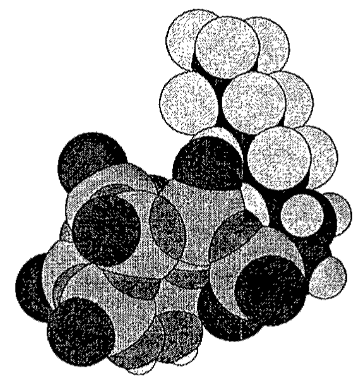
Alan Esker: POSS in thin films

Will answer fundamental question if POSS can diffuse through a matrix.

Alan Esker is in a position to finally Determine if the diffusion/surface Segregation of POSS is of significance.

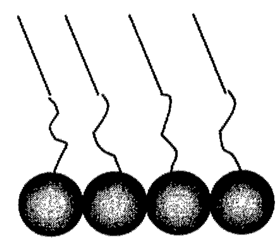
Experiments already underway (2+ years in the making for payoff)





Functionalized but still a surfactant!

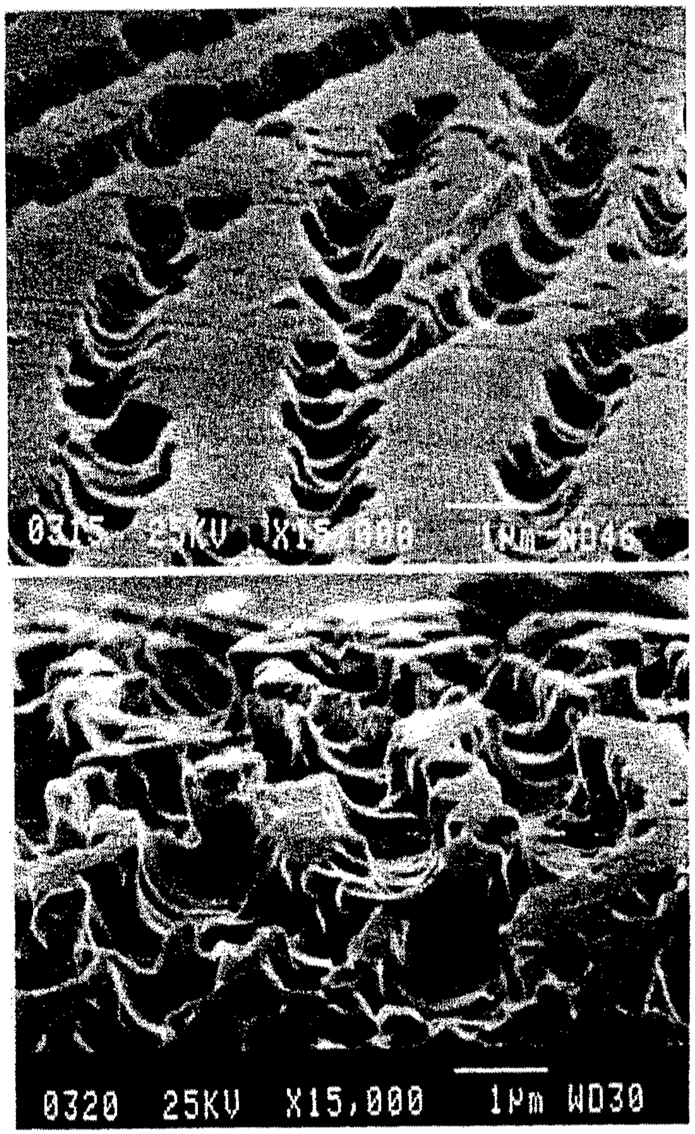
Can generate an "interfacial" region-compare to known self assembled surfactant structures

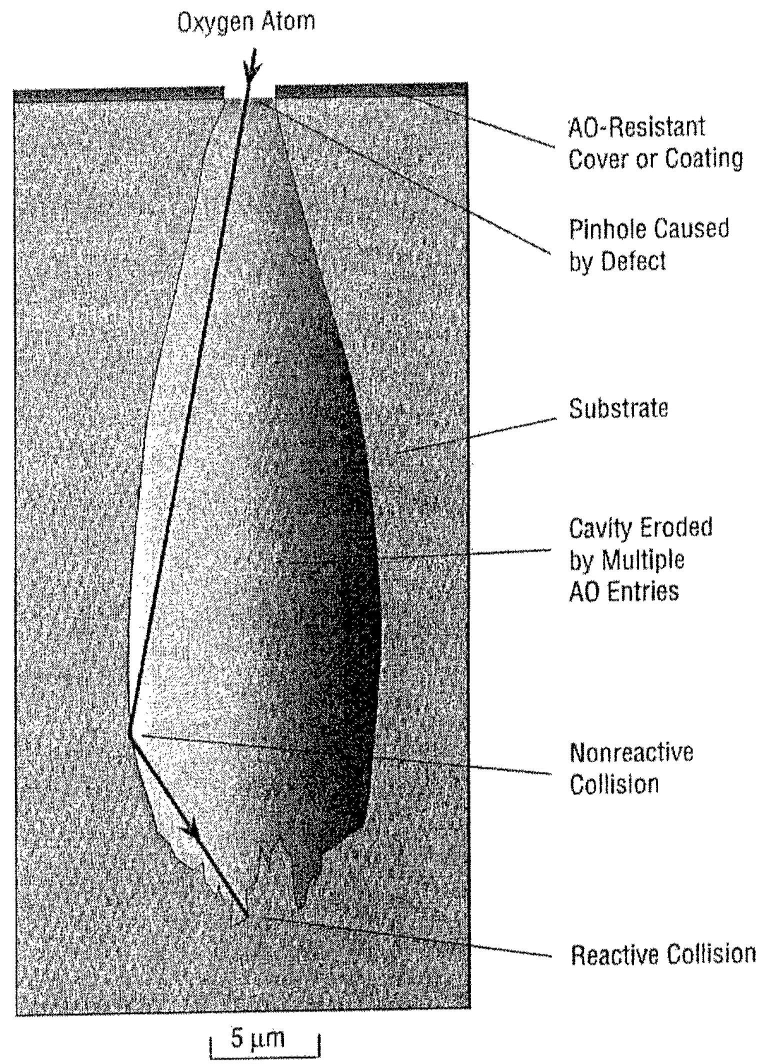


Esker, Viers JACS., 2002, in press.

Space Survivable Materials

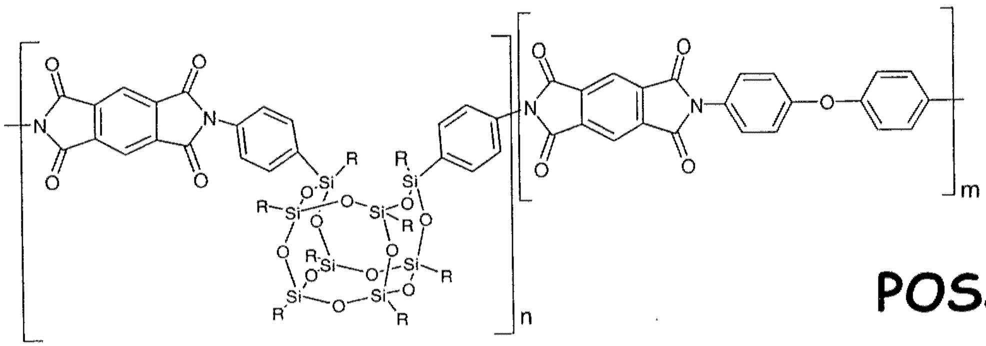
AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation



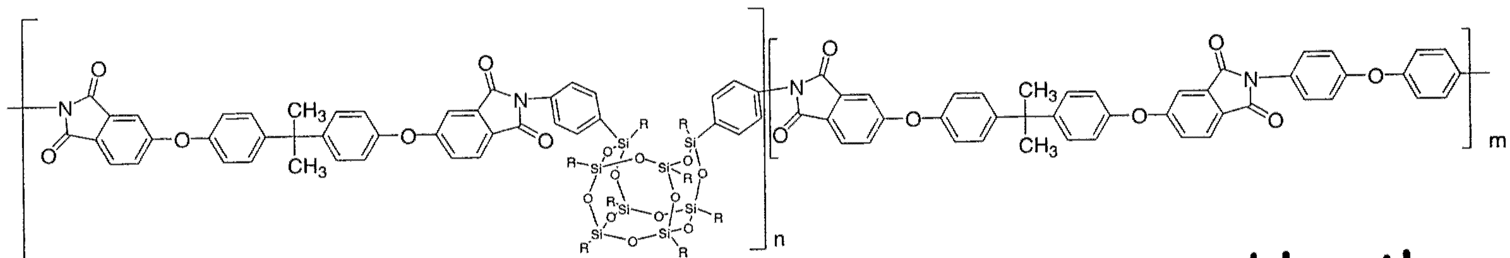


DeGroh, K.K., Banks, B.A., J. Spacecraft and Rockets, Vol. 31, No. 4, 656-664 (1994)

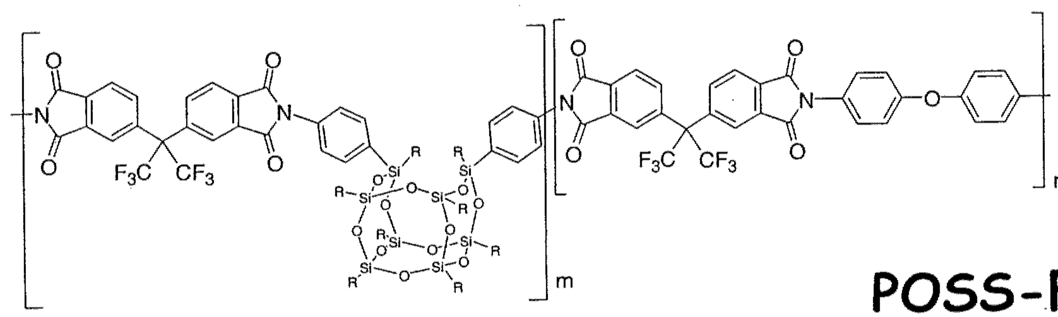
POSS High Performance Polyimides



POSS-Kapton polyimide

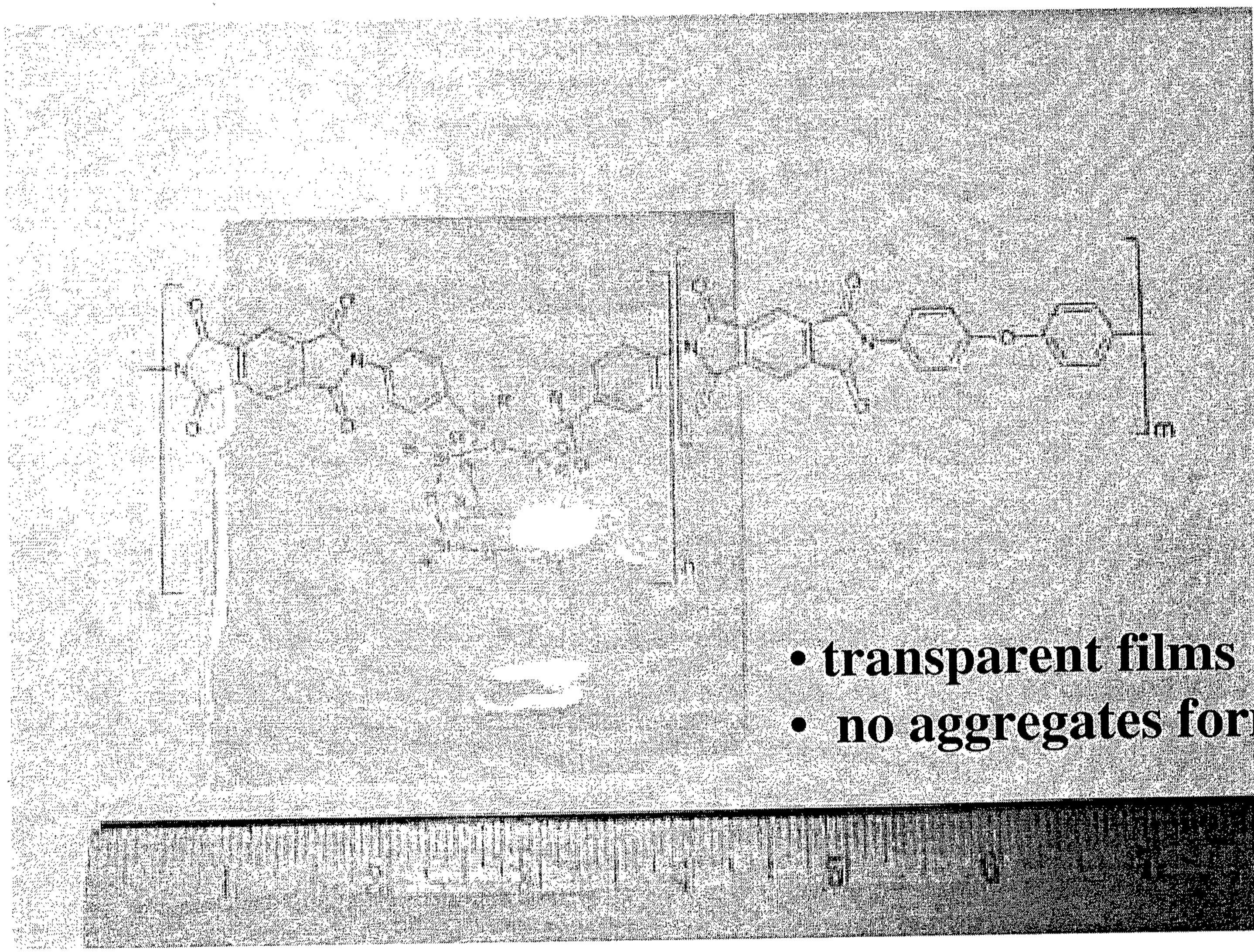


POSS processable ether-imide



POSS-Fluorinated colorless polyimide

POSS Kapton Polyimides



- transparent films
- no aggregates formed

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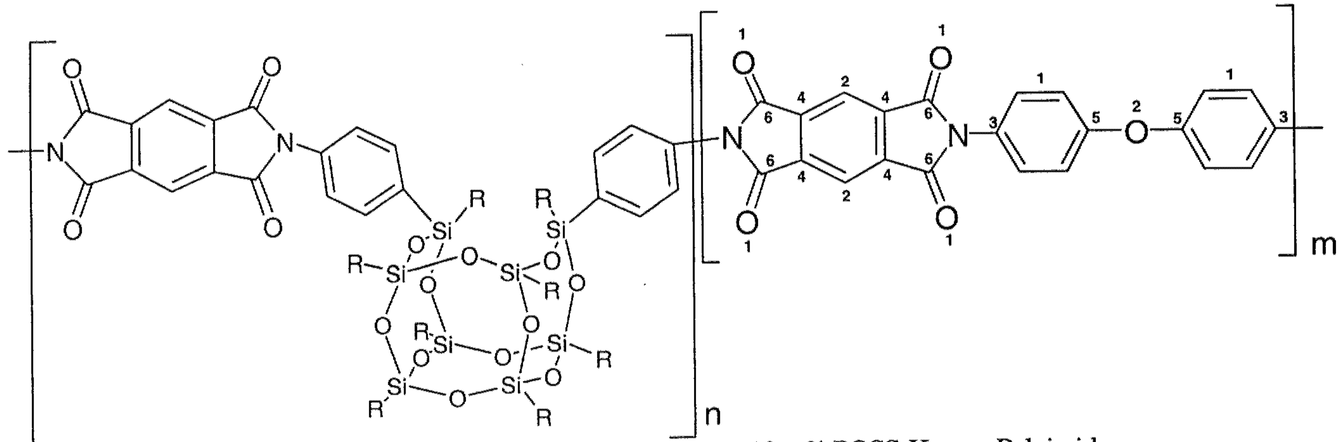
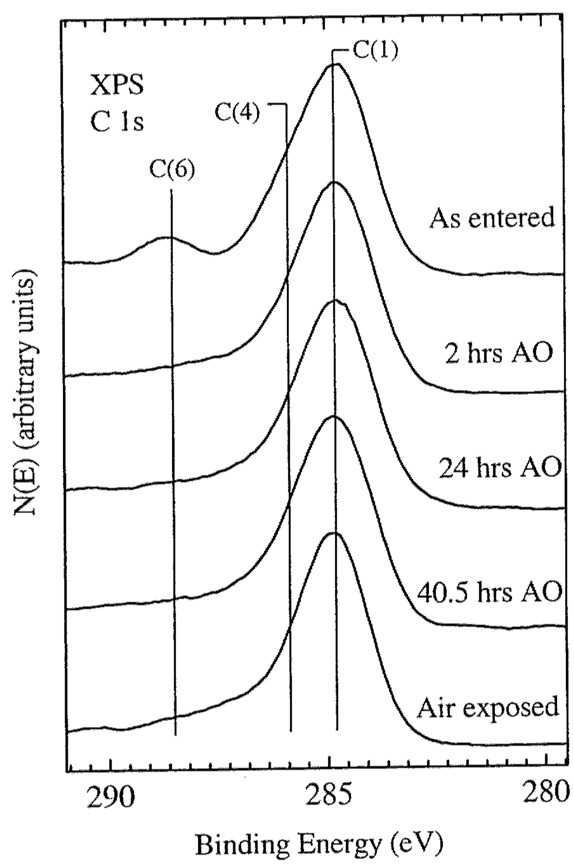
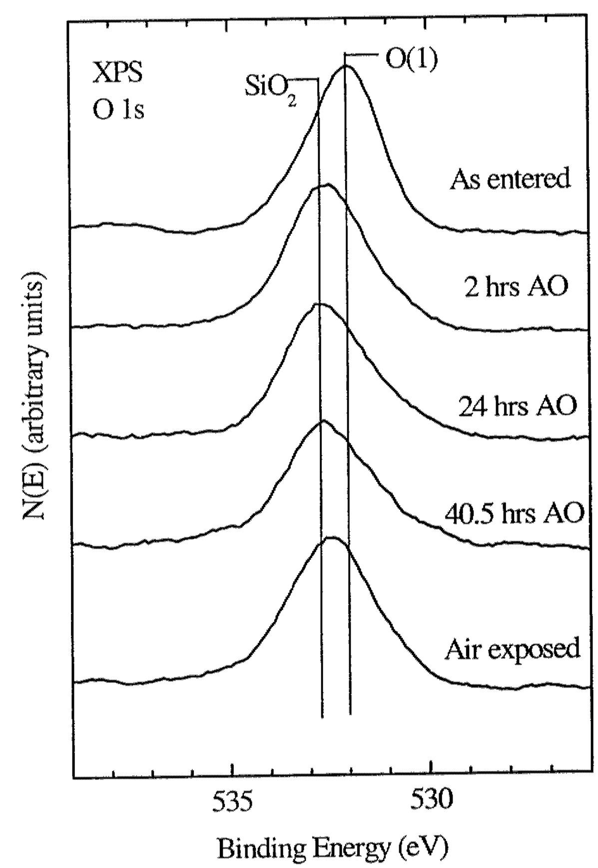
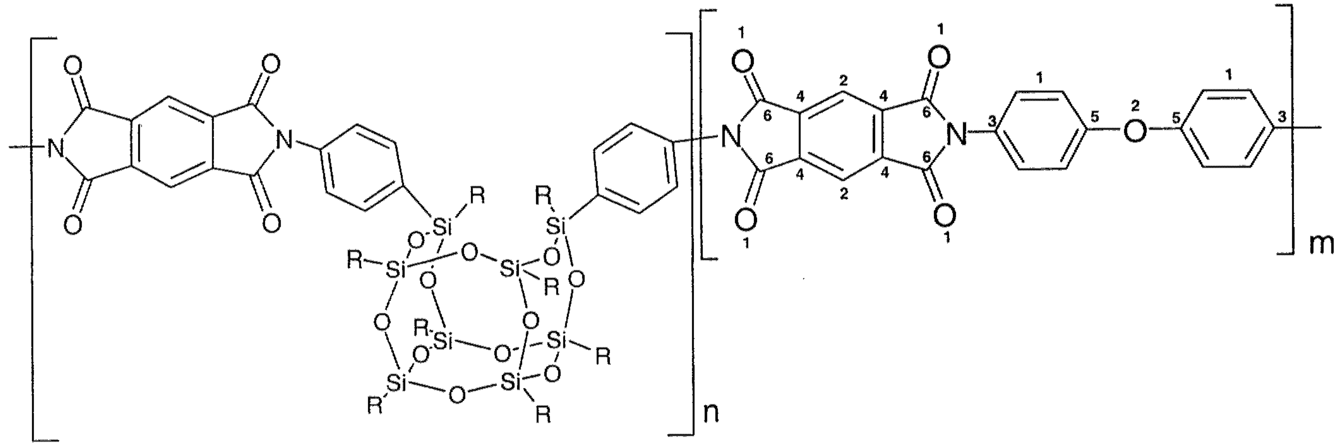


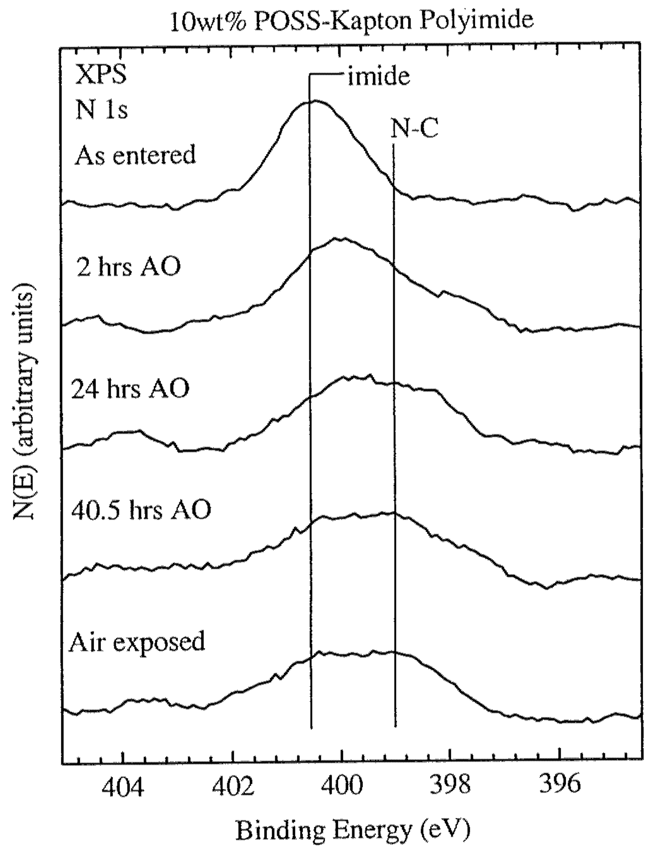
10wt% POSS-Kapton Polyimide

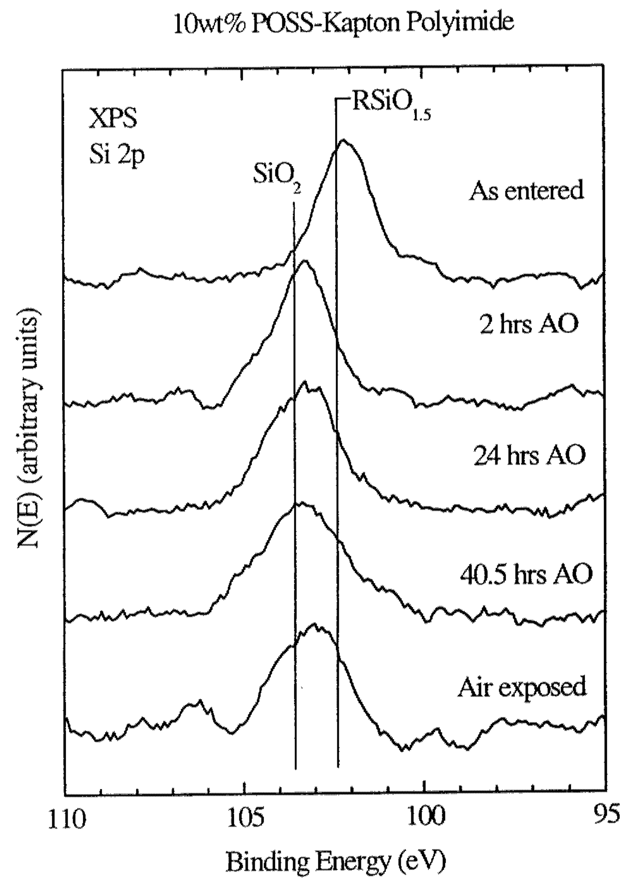


10wt% POSS-Kapton Polyimide

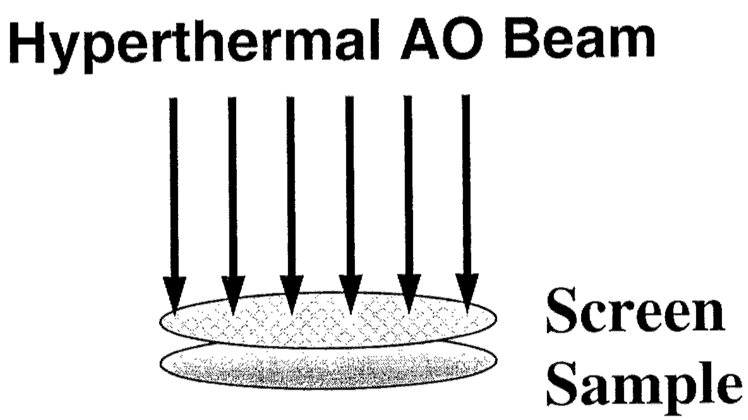


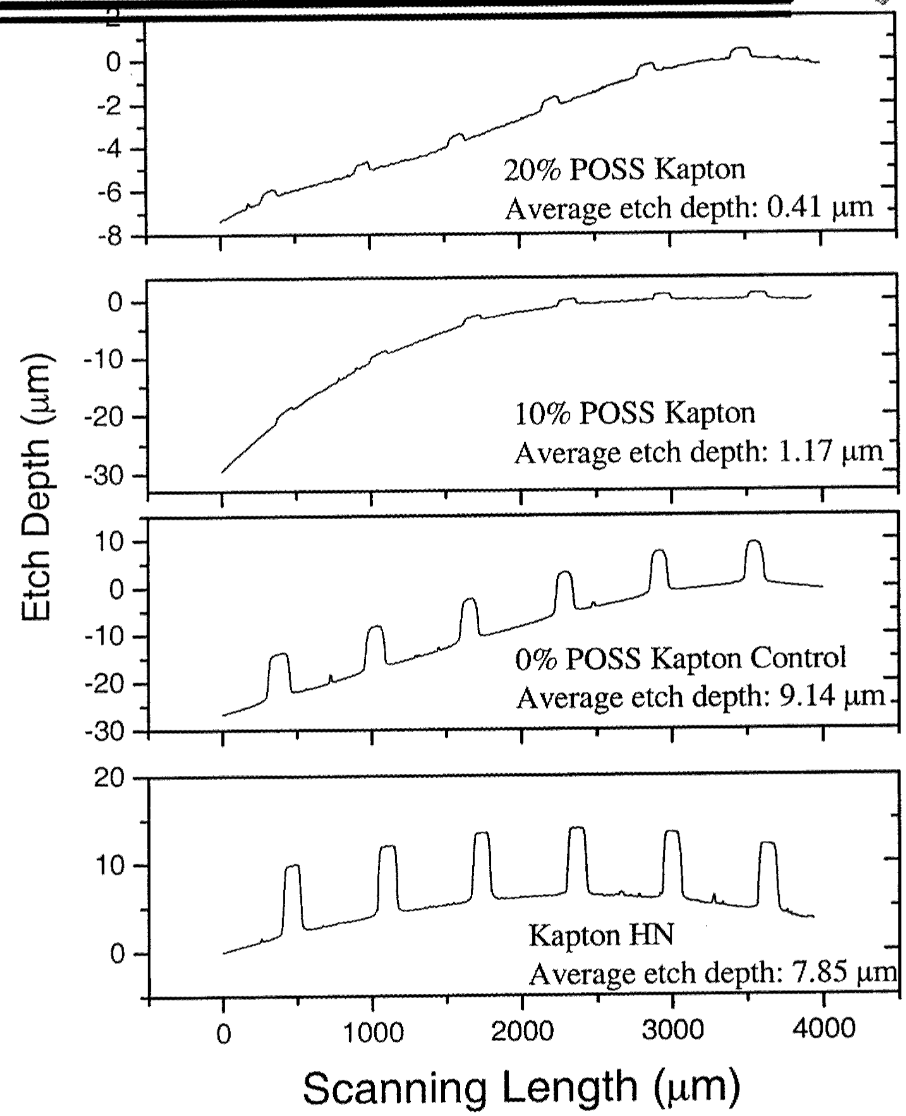



10wt% POSS-Kapton Polyimide
XPS
N 1s
imide
N-C
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
404
402
400
398
396
Binding Energy (eV)


10wt% POSS-Kapton Polyimide
XPS
Si 2p
RSiO1.5
SiO2
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
110
105
100
95
Binding Energy (eV)

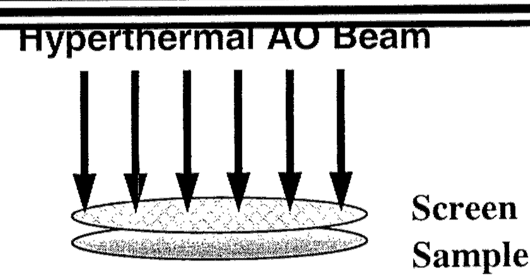
O-Atom etching experiment of POSS-Kapton polyimides
Total AO fluence of 2.62 x 10^{20} atoms/cm^2 (~ 3 Days in LEO)





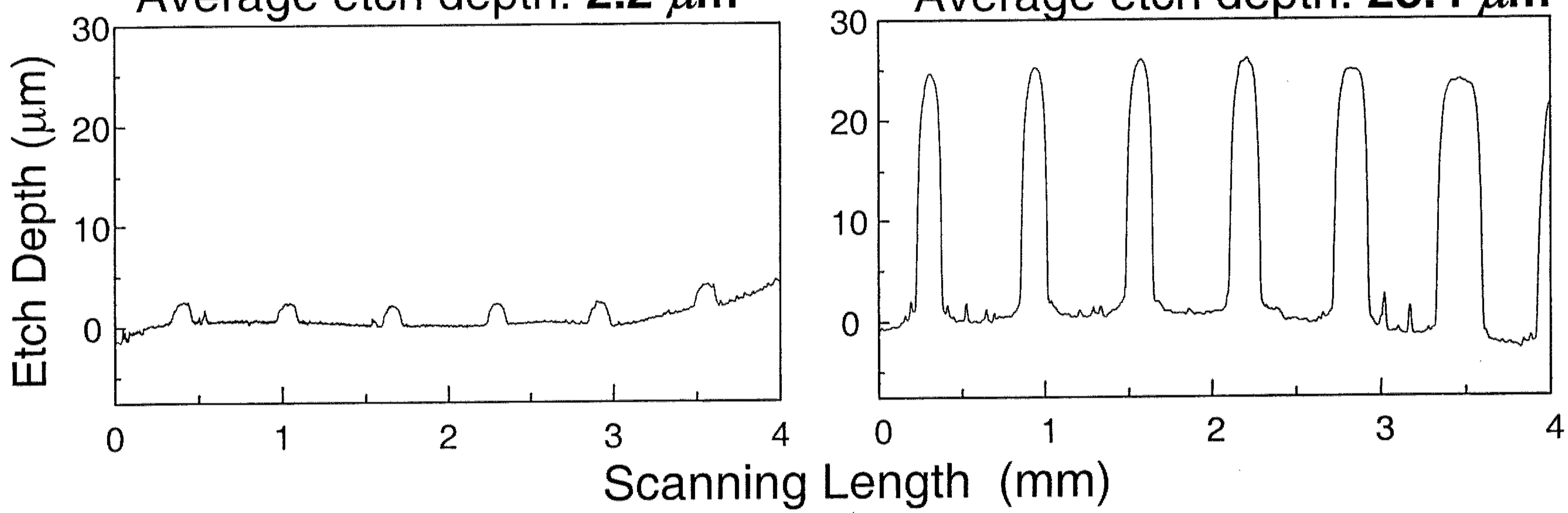
20 wt% POSS in Kapton results in over 20 time improvement in erosion resistance.

O-Atom Etching Experiment (~10 DAYS IN LEO)
Total AO fluence of 8.47×10^{20} atoms cm^{-2} (100,000 pluses)



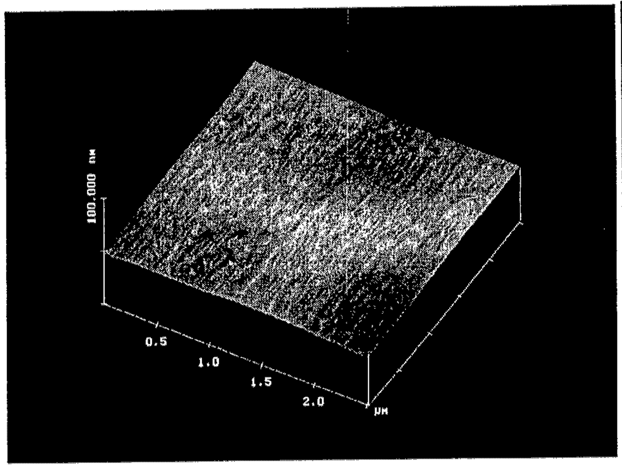
Kapton 10 wt% POSS — Average etch depth: **2.2 μm**

Kapton H Standard — Average etch depth: **25.4 μm**



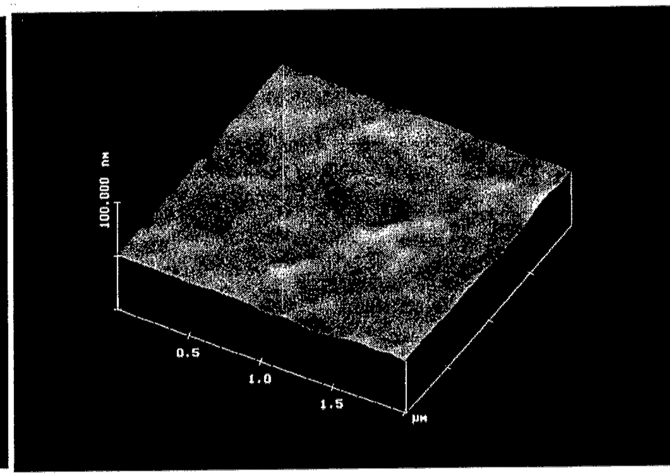
Significantly improved oxidation resistance due to a rapidly formed ceramic-like, passivating and **self-healing** silica layer preventing further degradation of underlying virgin polymer.

AFM Images of Unexposed POSS Polyimide Films



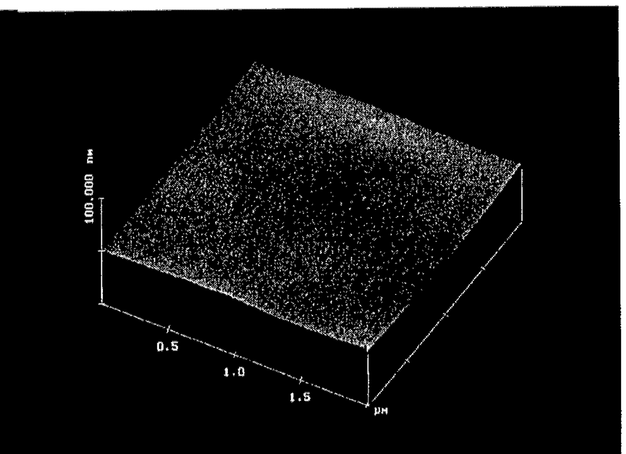
0% POSS

rms roughness: 1.09 nm



10% POSS

rms roughness: 1.03 nm



20% POSS

rms roughness: 1.55 nm

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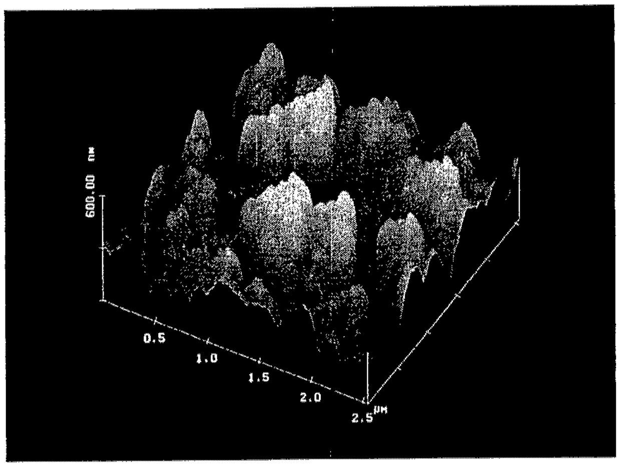
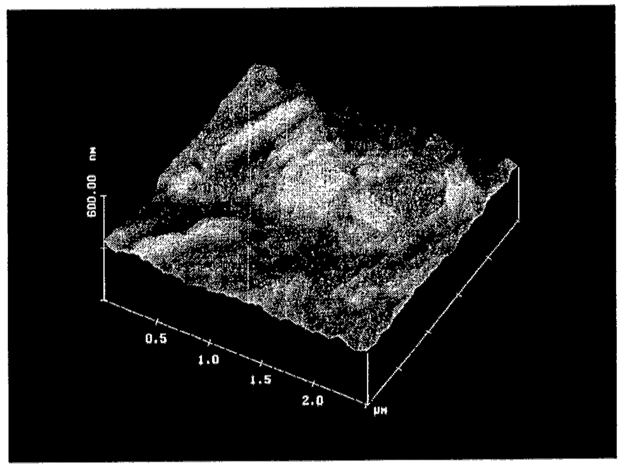
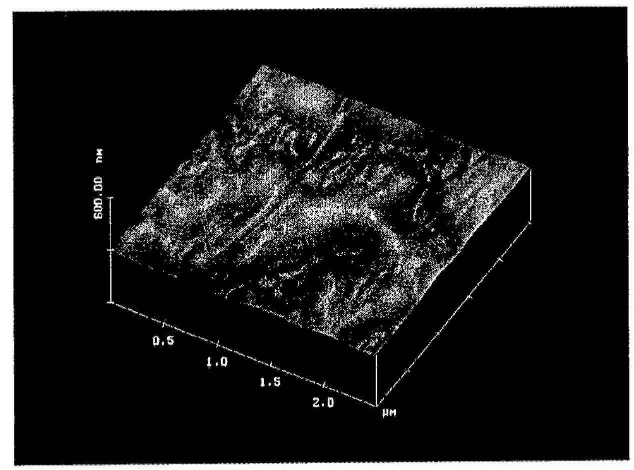
AFM Images of Exposed POSS Polyimide Films 100,000 Pulses of Hyperthermal (5 eV) AO Beam







0% POSS

rms roughness:
102 nm

10% POSS

rms roughness:
17.7 nm

20% POSS

rms roughness:
6.75 nm

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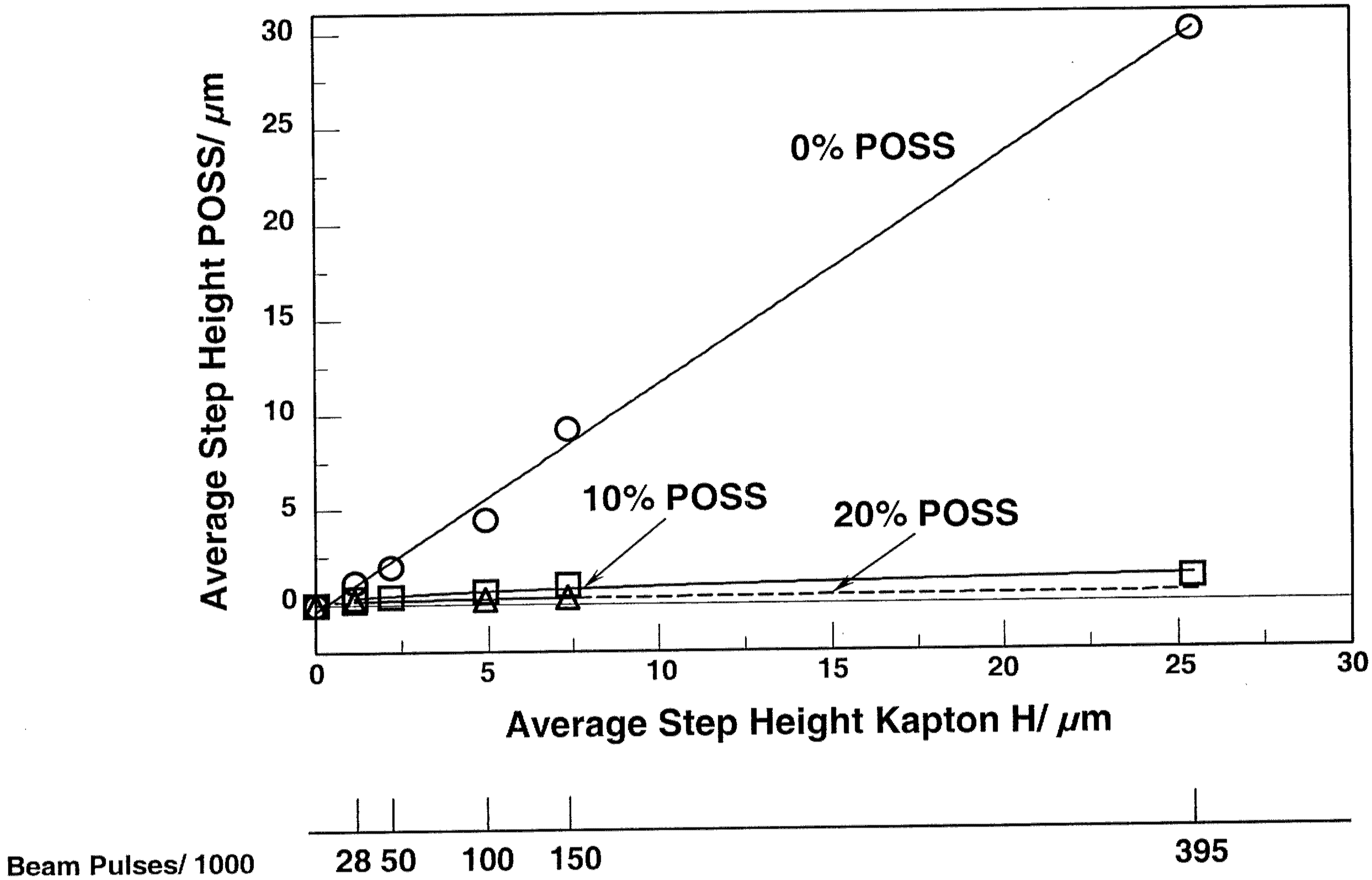
Erosion of POSS Polyimides by a Beam of Hyperthermal (5eV) O Atoms



Tri-collaborative Effort for Proposed High-Risk, High-Payoff Program (Industry, Academia & Government)

DARPA

POSS-Polymeric Materials Group
Materials Application Branch
AFRL, Edwards AFB

AIR FORCE RESEARCH LABORATORY

Hybrid Plastics™

TSI TRITON SYSTEMS INC

UNIVERSITY OF FLORIDA

MONTANA STATE UNIVERSITY BOZEMAN

THE AEROSPACE CORPORATION

Program Goals

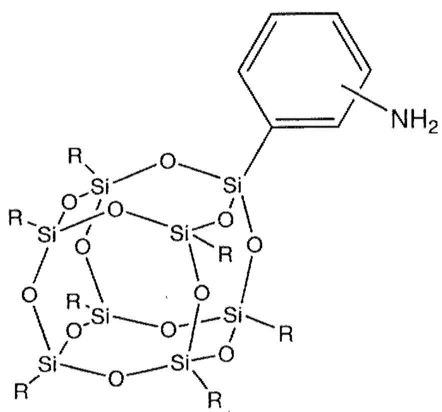
- The proposed program is based on the synthesis, development, characterization and testing of superior POSS-polyimide composite materials.

- Focus: Attainment of processable polyimides while retaining their high temperature stability and imparting enhanced space-survivability.

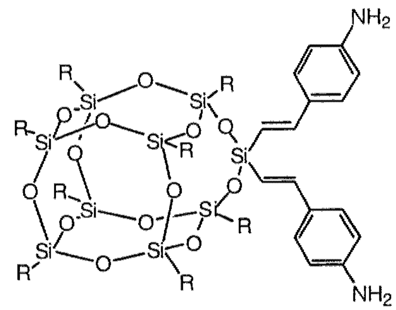
- Rapid Transition of POSS Polyimide Technology to Industry

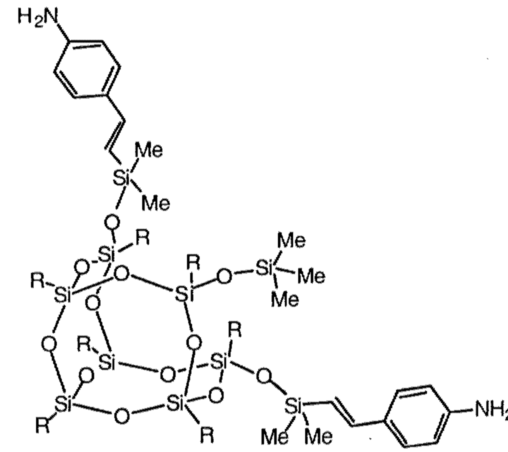
Cost Effective Route for POSS-Aniline Synthesis

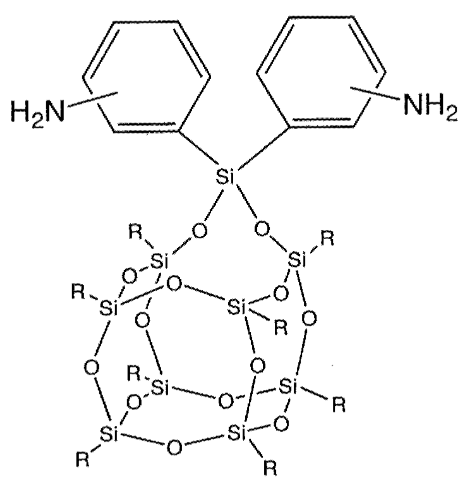
Hybrid Plastics™

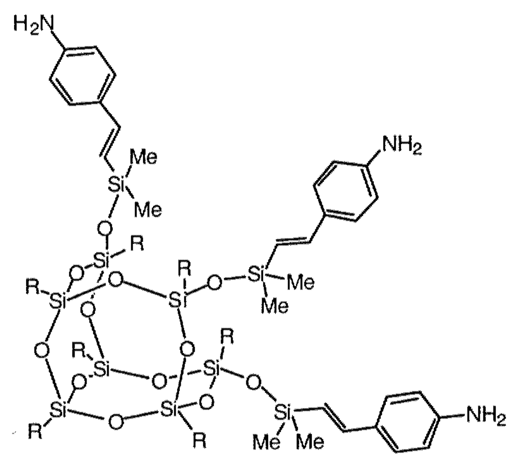


Cp_7T_8 aniline



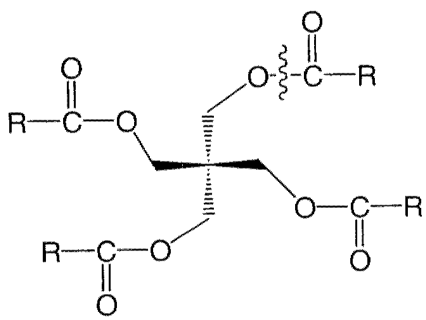




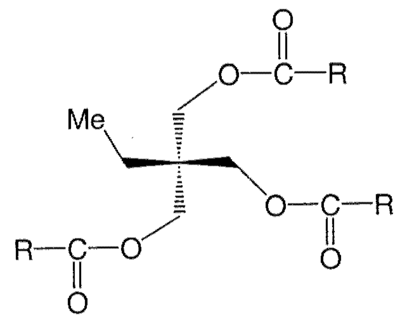


POSS Lubricants

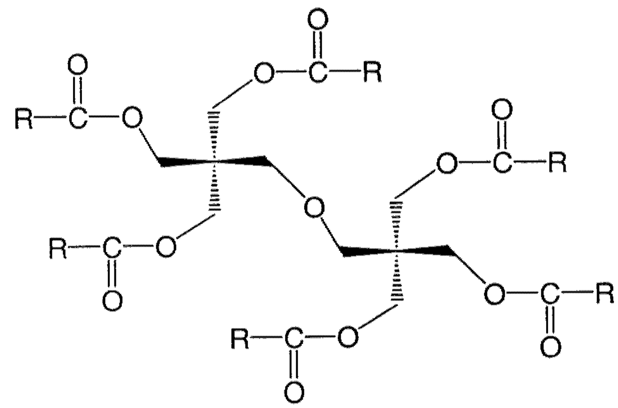
Present AF Lubricants Technology



Pentaerithritol Ester



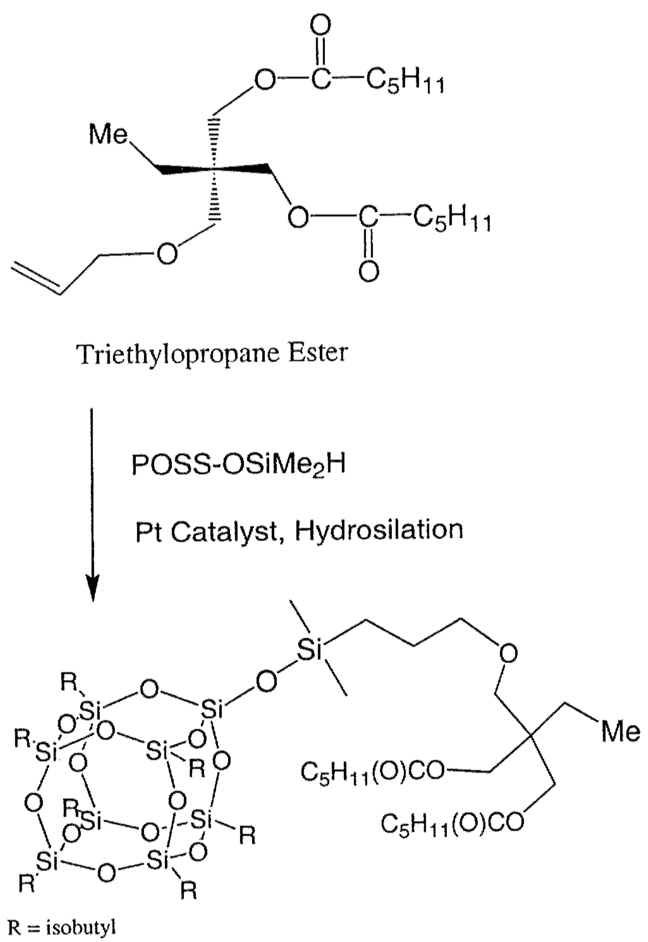
Trimethyloproane Ester



Pentaerithritol Dimer Ester

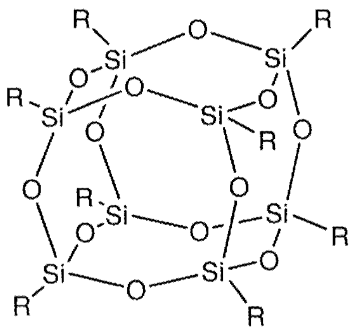
- The above polyol ester compounds are the main components of some AF turbine lubricants
- Operating range of –40 °C to 200 °C
- Aminic antioxidants used

POSS Diesters as Lubricants

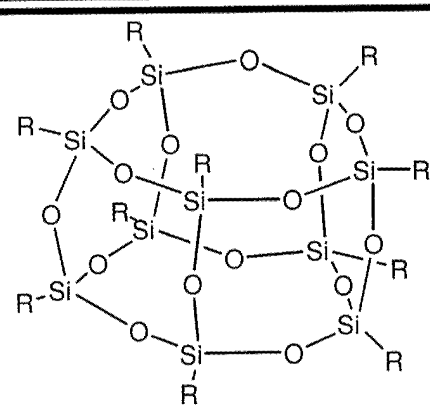


- One possible approach for lubricants is the use of a heat sink: POSS may be usable in this capacity
- 3 grams made to prove concept
- Research problems (separation of unreacted TMP diester from POSS diester was not trivial due to similar solubilities) were overcome: vacuum distillation!
- Waxy Solid at room temperature
- Solubility in Grade 4 ester base stock: High, can be used in additive testing
- Further Physical testing will be done shortly

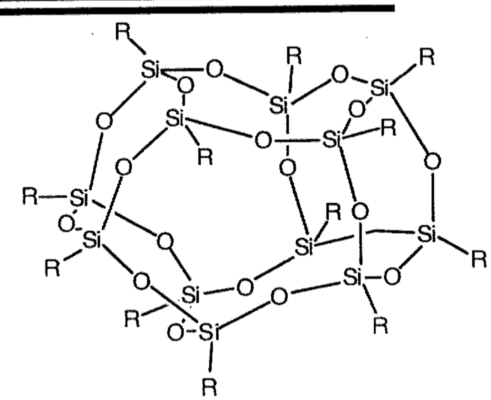
Isooctyl$_n$T$_n$ as a Lubricant



R = **Isooctyl**
major component



R = **Isooctyl**
minor component

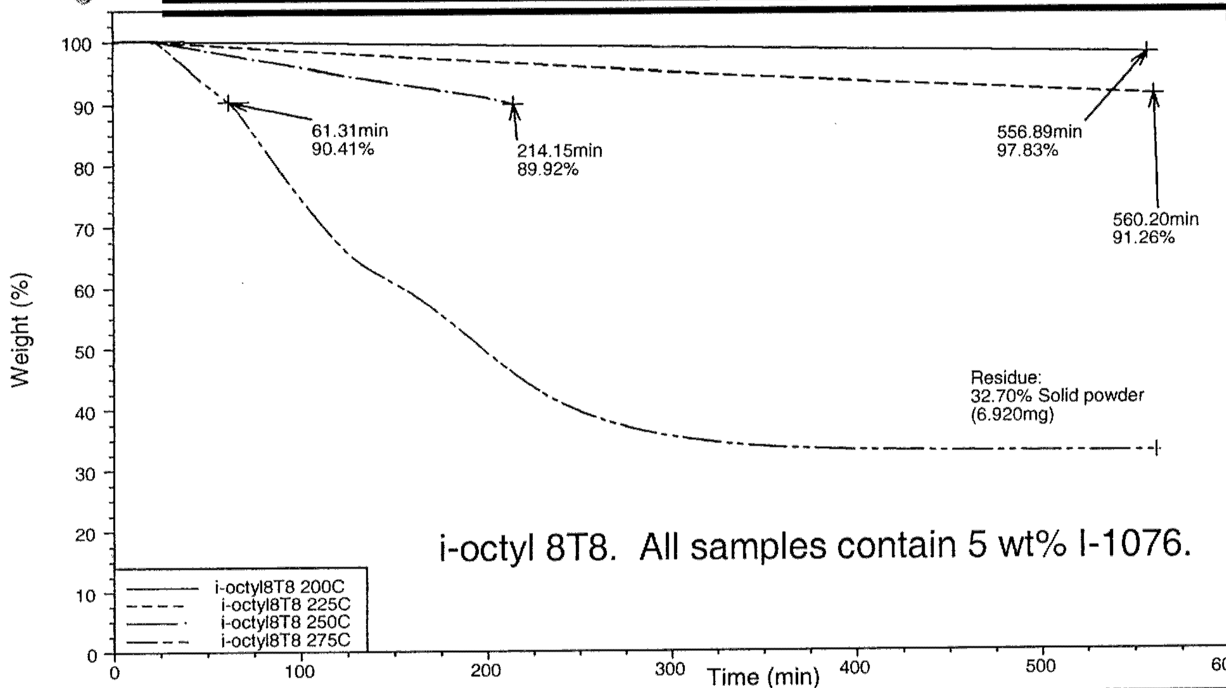


R = **Isooctyl**
minor component

- Advantages:
- Commercially available; relatively low cost.
- Proven stability under nitrogen to 275 ºC without volatilization

- Accomplishments:
- Resin inherent in sample removed by distillation!
- AF Aminic AOs decompose POSS so compatible phenolic AO used

TGA of Isooctyl$_n$T$_n$ w/AO



Temp °C	Vis cP
20	13100
30	7950
40	3100
50	1600
60	725
80	260
90	166
100	112.6
110	79
120	57
130	44
140	32
150	25
160	20.4
170	16.3
180	13.8

Material	TGA temp	TGA temp	Time to 10% mass loss	% lost after 9 hrs	residue
POSS Diester	200 °C	392 °F	4.6 hr	Stopped @ 4.6hrs	Solid
POSS Diester w/ AO	200 °C	392°F	7.5 hr	11	Solid
Isooctyl$_n$T$_n$ with 5% I-1076	200 °C	392 °F	--	2.2	Oil
Isooctyl$_n$T$_n$ with 5% I-1076	225 °C	437 °F	--	9.0	Oil
Isooctyl$_n$T$_n$ with 5% I-1076	250 °C	482 °F	3.5 hrs	Stopped @ 3.5hrs	Oil
Isooctyl$_n$T$_n$ with 5% I-1076	275 °C	527 °F	1hr	70	Grit

FY03 6.1 Future Direction

- Focus internal & collaborative work on specific polymer systems
  - Complete story on **POSS-PN**
  - Fully develop **POSS-PS** glassy polymer story
  - Begin **POSS-Kraton** TPE
  - Quantify blends vs. copolymer property enhancements (**POSS-PS**, **POSS-Kraton**)
- Develop definitive models for specific polymer systems
  - TEM, AFM = pictures of structure
  - Physical/mechanical data = structure/property relationship

Complete story on POSS PN

- Synthesis of POSS-PN polymers containing Ethyl & Phenyl R groups
- Obtain TEM images of polymers
- Obtain mechanical properties of polymer systems
- Compare data to refine Coughlin Model

Does new model apply to other polymer systems?

Fully develop POSS *glassy* polymer story

- With understanding obtained from POSS-PN, fully characterize high molecular weight PS
  - cyclohexyl, isobutyl & ethyl co-polymers need to be synthesized
  - rheology, DMTA data
  - Obtain TEM, AFM images
  - Develop structure/property relationship
  - Apply Coughlin model to glassy polymers

Does new model apply to other polymer systems?

Develop POSS TPE Model

- Synthesize POSS-Kraton polymers
  - Develop POSS-hydride monomers with variable R groups
  - Graft onto Kraton
  - Rheology/DMTA data
  - Obtain TEM/AFM images
  - Develop structure/property relationship
  - Apply Coughlin model to TPE polymers

Does new model apply to other polymer systems?

Blends & Copolymers

- POSS-PS (MIT Durint)
  - MIT group with perform blends work
  - Compare with our ongoing POSS-PS copolymers
  - Quantify results and develop model
- POSS-Kraton
  - Andre Lee will perform rheological/DMTA data on blends and copolymers synthesized in-house
  - Quantify results and develop model

Compare POSS-PS to POSS-Kraton?

3-Year Plan

- Quantified property enhancements of POSS for POSS-PN, POSS-PS, POSS-Kraton
- Develop a working model or models that defines the role of POSS-POSS and POSS-polymer interactions for all types of polymers systems (e.g., glassy, rubbery, semi-crystalline, thermoset)